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## PARTIAL CONTENTS

	Page
ON THE CAUSES OF THE OXIDATION OF URANIUM IN URANINITES, by V. I. Lebedev .....	1
THE ENTRY OF URANIUM INTO SOME ROCK- FORMING MINERALS, by I. G. Chentsov .....	5
THE SALT BALANCE OF THE ARAL SEA, by L. K. Blinov .....	26
NATURE OF NAPHTHENIC ACIDS IN BAKU CRUDE OILS AS A FUNCTION OF THE DEPTH OF OCCURRENCE, by G. G. Ashumov .....	42
REFERENCE SECTION .....	78

- complete table of contents inside -

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## CONTENTS

	Page
TRANSLITERATION OF RUSSIAN . . . . .	ii
THE CAUSES OF THE OXIDATION OF URANIUM IN URANINITES, by V. I. Lebedev, translated by Royer and Roger, Inc. . . . .	1
ENTRY OF URANIUM INTO SOME ROCK-FORMING MINERALS, by I. G. Chentsov, translated by Michael Fleischer . . . . .	5
GEOCHEMISTRY OF TANTALUM AND NIOBIUM, by M. V. Kuzmenko, translated by Michael Fleischer . . . . .	9
SALT BALANCE OF THE ARAL SEA, by L. K. Blinov prepared by Research International Associates . . . . .	26
OF NAPHTHENIC ACIDS IN BAKU CRUDE OILS AS A FUNCTION OF THE DEPTH OF OCCURRENCE, by G. G. Ashumov, translated by Royer and Roger, Inc. . . . .	42
CERTAIN RELATIONSHIPS IN THE COMPOSITION OF CRUDE OIL, by A. F. Dobryansky, P. F. Andreyev and A. I. Bogomolov, translated by Royer and Roger, Inc. . . . .	49
EXPERIMENTAL STUDIES OF COMBUSTION IN OIL SANDS, by A. B. Sheinman and A. I. Sergeev, translated by Royer and Roger, Inc. . . . .	60
GEOLOGY AND TECTONICS OF THE KUZBAS, by P. M. Gorshkov . . . . .	69
FEASIBLE NEW METHODS OF PROSPECTING AND EXPLORATION (Summary of award-winning papers submitted in competition to the Ministry of Geology and Conservation of Mineral Resources of the U.S.S.R.), by N. G. Zhilkin, translated by Eugene A. Alexandrov . . . . .	71

## REFERENCE SECTION

ASIAN AND EAST EUROPEAN GEOLOGIC ACCESSIONS OF THE LIBRARY OF CONGRESS, October-November 1960 . . . . .	78
RECENT TRANSLATIONS IN GEOLOGY . . . . .	85
GEOLOGIC TRANSLATIONS FROM THE PUBLIC LAW 480 PROGRAM OF THE NATIONAL SCIENCE FOUNDATION . . . . .	89

## IGR transliteration of Russian

The AGI Translation Office has adopted the essential features of Cyrillic transliteration recommended by the U. S. Department of the Interior, Board on Geographic Names, Washington D. C.

However, the AGI Translation Office recommends the following modifications:

1. Ye initially, after vowels, and after ъ, ѣ. Customary usage calls for "ie" in many names, e. g., SOVIET KIEV, DNEPER, etc.; or "ye", e. g., BYELORUSSIA, where "e" follows consonants. "e" with dieresis in Russian should be given as "yo".
2. Omitted if preceding a "y", for example, Arkhangel'sky (not "iy"; not "ii").
3. Generally omitted.

NOTE: Well-known place and personal names that have wide acceptance will be used. Some translations may include elements of previous German transliteration from the Russian; this occurs in IGR most commonly in maps and lists of references. The reader's attention is called to the following variations between German and English systems which may cause confusion when trying to check back to original Russian sources.

Alphabet	transliteration	
А	а	a
Б	б	b
В	в	v
Г	г	g
Д	д	d
Е	е	e, ye <sup>(1)</sup>
Ё	ё	ë, yë
Ж	ж	zh
З	з	z
И	и	i <sup>(2)</sup>
Й	й	y
К	к	k
Л	л	l
М	м	m
Н	н	n
О	о	o
П	п	p
Р	р	r
С	с	s
Т	т	t
У	у	u
Ф	ф	f
Х	х	kh
Ц	ц	ts
Ч	ч	ch
Ш	ш	sh
Щ	щ	shch
Ъ	ъ	" <sup>(3)</sup>
Ы	ы	y
Ь	ь	" <sup>(3)</sup>
Э	э	e
Ю	ю	yu
Я	я	ya

German	English
w	v
s	z
ch	kh
tz	ts
tsch	ch
sch	sh
schtsch	shch
ja	ya
ju	yu

## TENTATIVE CONTENTS FOR THE FEBRUARY 1961 ISSUE

AUTOMETASOMATIC ALTERATION OF GRANITOIDS AND ASSOCIATION OF TIN MINERALIZATION WITH THE ZONE OF SODIUM-POTASSIUM METASOMATISM, by V. A. Serebryakov.

METHODS OF MERCUROMETRIC INVESTIGATIONS, by E. A. Sergeev

CLIMATE AND OIL GENESIS, by L. A. Nazarkin

SYNGENESIS AND EPIGENESIS IN PETROGRAPHY AND THE STUDY OF MINERAL DEPOSITS, PART 1 of 2, by G. C. Amstutz

THE RIDDLE OF TEKTITES, by G. G. Vorobyev

NOTE: The "Tentative Contents" list in v. 2, no. 12, was headed "for the January 1960 Issue." The year should have been 1961



# THE CAUSES OF THE OXIDATION OF URANIUM IN URANINITES<sup>1</sup>

by

V. I. Lebedev<sup>2</sup>

• translated by Royer and Roger, Inc. •

## ABSTRACT

This article introduces a refinement into calculations of absolute geologic age by the uranium-isotope method, by showing that the overall rate of auto-oxidation of uranium in uraninites is accelerated in the peripheral parts of uraninite crystals, and that the age determinations based on radioactive decay of uraninite are thus somewhat exaggerated. In the outer layers of the crystals, from which  $\text{He}^{++}$  ions and  $e^-$  electrons can escape into the surrounding medium, the rate of oxidation of uranium, and hence of its ultimate transformation into lead, is increased by the dissociation of water and absorption of  $\text{O}^{2-}$  ions by uranium and lead cations, through the action of escaping  $\alpha$ - and  $\beta$ - radiation. Under certain conditions the processes in the intensively oxidized outer layers may also involve reduction of some  $\text{UO}_3$  to  $\text{UO}_2$ , and the secondary formation of galena segregations when  $\text{H}_2\text{S}$  is present, in the surrounding solutions. --P. T. Broneer.

\*\*\*

V. A. Leonova recently published a detailed paper on the mineralogy and crystal chemistry of the uraninites of Northern Karelia (Leonova, 1959). This paper discussed the extremely important problem of the oxidation of uranium. A. Leonova, after reviewing the earlier investigations (Komlev, 1957; Khlopin, 1938), came to the following conclusions:

"The oxidation of the Karelian uraninites is a combined result of several processes:

"a) primary oxidation of the uranium during crystallization of the uraninite;

"b) crystallochemical compensation in the replacement of  $\text{U}^{4+}$  by  $\text{RE}^{3+}$  and other ions with small electrical charges, accompanied by the introduction of a corresponding number of  $+$  ions into the uraninite crystal lattice;

"c) auto-oxidation of the uraninite in the course of radioactive decay of the uranium and formation of Pb;

"d) subsequent oxidation of the uraninite; this process is accompanied by the loss of part of the uranium in maintaining a constant amount of oxygen in the uraninite lattice.

"Processes 'a' and 'b' evidently play a small role in the general scheme of the oxidation of uraninite.

"The uranium loss in the Karelian uraninites fluctuates between 0.5 and 15.8 percent."

As a result of this loss of uranium, there is a formation of secondary uranium minerals containing  $\text{UO}_2^{++}$  -- curite, clarkeite, soddyite, uranophane, etc. (Leonova, 1959).

It is easy to see that these conclusions are of very great significance. For example, from the last conclusion 'd' alone, it follows that all the age determinations made thus far from the ratio of radiogenic lead to undecayed uranium are greatly exaggerated. On the other hand, in spite of the abundant evidence supporting the majority of these conclusions, the problem of the reasons for the oxidation of uranium in uraninites cannot, in general, be considered fully solved.

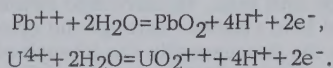
Without making a detailed examination of processes 'a' and 'b', whose importance in uraninites is actually very small, it may be noted that they do, however, definitely occur. In addition, the first process is probably typical of the superficially non-crystallized uraninites which are usually formed under hydrothermal conditions -- the uranium pitchblende in which the  $\text{UO}_2^{++}$  may be considered as being trapped in a structure of the uraninite type during crystallization according to the scheme suggested by G. B. Naumov -- that is, in the process of reduction (Naumov, 1959). As regards the second process, it may be supposed that this plays an even smaller role than would follow from the quantity of RE since a certain amount of the RE is of secondary origin and makes up the greater part of the group of heavy elements arising in the decay of uranium. A group of light elements, represented mainly by Sr and Y, should also appear in equivalent amount.

Process 'c' (auto-oxidation of uraninite), according to the formula (the Kirsch-Khlopin re-

<sup>1</sup>Translated from *O prichinakh okisleniya urana v uraninitakh*; *Zapiski Vsesoyuznogo Mineralicheskogo Obshchestva*, v. 88, no. 6, p. 667-671, 1959. Technical content reviewed for IGR by Clifford Frondel.



action)  $2\text{UO}_2 \rightarrow \text{PbO} + \text{UO}_3 + 8\text{He}$ , which was derived earlier as the basis of the oxygen method (the  $\text{UO}_3/\text{UO}_2$  ratio) of determining geologic age (Khlopov, 1938), undoubtedly does take place. But one of the arguments cited in refuting the Wasserstein hypothesis (that formed part of the basis for the radiometric method of age determination), which considered that  $\text{PbO}_2$  is present in uraninites and thorianites -- specifically, the reference to the oxidation-reduction potentials of  $\text{PbO}_2$  and  $\text{UO}_2^{++}$  -- has turned out to be ephemeral.<sup>3</sup> The oxidation-reduction potentials of these compounds, which are 1.46v and 0.42v respectively, refer specifically to the reactions occurring in solution:

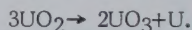


For this reason, the corresponding amount of  $\text{UO}_3$  instead of  $\text{UO}_2$  as obtained in chemical analysis may indicate merely the formation of  $\text{UO}_2^{++}$  at the moment of radioactive decay of the uraninite, as the electrons drop to  $\text{Pb}^{4+}$ , and of  $\text{H}_2\text{O}$  (Lebedev, 1957) and its subsequent reaction with the water, with the formation of  $\text{UO}_2(\text{OH})_2$ .

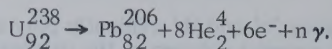
The actual proof of the auto-oxidation of uranium in uraninites, by the Kirsch-Khlopov reaction, is the magnitudes of the  $a$  lattice parameters of the uraninites (Leonova, 1959), inasmuch as the presence of  $\text{Pb}^{++}$  must increase them considerably. This proof is especially convincing if one compares the parameters of these uraninites with those of pitchblendes that contain much smaller or no amounts of Pb in their crystal structure. On the average, the  $a$  parameters in the uraninites are 0.04 - 0.05 Å greater than in the pitchblendes with similar  $\text{UO}_3$ -to- $\text{UO}_2$  ratios (Sidorenko, 1958).<sup>4</sup> To this proof one might add one more argument, derived from the properties of chemical elements that determine their position in the Mendeleev Table and its laws. It is known that the bonding energy of the s-electron regularly increases from period to period after the empty spaces in the d-electron levels have been filled (down the Cu, Zn -- Ag, Cd -- Au, Hg columns), and especially after the vacancies in the f-level

(Au and Hg) have been occupied (Lebedev, 1957, Schchukarev, 1954).<sup>5</sup> For this reason Tl most often occurs in nature in univalent form, and for the same reason Pb and Bi, which are next in line after it, tend to be bi- and trivalent, rather than quadri- and quinquevalent, respectively. This increase in the strength of the bond between the s-electrons and the Pb atom is well illustrated by the heats of formation of  $\text{PbO}$  and  $\text{PbO}_2$ , which are equal to 52.3 and 64.3 kcal respectively, as compared to the heats of formation of their closet analogs  $\text{SnO}$  and  $\text{SnO}_2$ , which are respectively 67.9 and 137.8 kcal. The increase in the heat of formation of  $\text{PbO}_2$  by 12 kcal, as compared to  $\text{PbO}$  -- that is, by an amount which only slightly exceeds the decrease in the entropy of free  $\text{O}_2$  (Lebedev, 1957, p. 172) -- testifies to the low stability of  $\text{PbO}_2$  and the existence of a compound in which oxygen is bound with greater energy, in the case  $\text{UO}_2$ .

There is no doubt of the occurrence of still one more process of oxidation of the uranium in uraninites. The considerable increase in the content of  $\text{UO}_3$  relative to the equivalent amount of  $\text{PbO}$  (Komlev, 1957; Soboleva and Pudovkina, 1957; Leonova, 1959) is the proof of this. This process, however, is scarcely one of subsequent loss of uranium ("in any form") to correspond with the constant quantity of oxygen postulated by the formula:



It is well known that the radioactive decay of uranium is a very complicated process (Ran-kama, 1956). In the course of transformation of an atom of U into an atom of Pb and eight atoms of He, such elements with high migration capabilities as Ra and Rn are formed. The lead itself, in the form of  $\text{Pb}^{++}$ , not to mention He, is much more highly mobile than, for example,  $\text{U}^{4+}$ , a multiple charged cation with an electrostatic bonding energy some five times greater than that of  $\text{Pb}^{++}$ . In spite of this fact in minerals that do not undergo any noticeable change as a result of secondary mineral-forming processes the overall radioactive decay of uranium in the nuclear reaction may be represented as follows:



The outer shell of the U atom contains 92 electrons, and there are 98 electrons in that of a Pb atom and eight He atoms. This means that the six electrons that are liberated, or the  $\beta$ -radiation, are absorbed by helium ions, or  $\alpha$ -particles. It is known that the  $\alpha$ -particle

<sup>3</sup> The ephemeral nature of this argument is seen in the fact that, in spite of the respective oxidation-reduction potentials, in titanomagnetite, aegirite and certain other minerals  $\text{Fe}^{3+}$  is accompanied by  $\text{V}^{3+}$ , but not  $\text{V}^{4+}$ , whereas in certain garnets (schorlomite) it is accompanied also by  $\text{Ti}^{3+}$ , and not only by  $\text{Ti}^{4+}$  (Shcherbina, 1946).

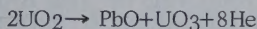
<sup>4</sup> G.A. Sidorenko, without regard to the different contents of Pb in uraninites and pitchblendes, suggests that the reason for such a considerable difference in the parameters "probably lies in their genetic peculiarities."

<sup>5</sup> This causes compression of the electron shell and raises the ionization potential of the s-electrons.

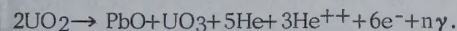


expelled from the uranium nucleus has great kinetic energy (2.34 - 10.54 mev) and ionization capability. In the crystal lattice the  $\alpha$ -particle expelled from the nucleus acts upon  $10^3$  -  $5 \cdot 10^3$  atoms and penetrates to a distance of 0.02 - 0.05 mm. The  $\beta$ -particles also have a considerable ionization capability (with an energy of 0.35 - 2.62 mev). Their ability to penetrate is, on the average, some 100 times greater than that of  $\alpha$ -particles. The  $\gamma$ -radiation (whose energy is 0.01 - 3.0 mev) also has great ionizing capability and great penetrating power, and when hindered causes the appearance of electrons of internal conversion (secondary electrons) (Rankama, 1956).

From these facts it will readily be concluded that if one takes a small crystal of uraninite, about 1 cm in cross section, the overall auto-oxidation reaction



will not reflect the actual occurrences in its peripheral parts. In the periphery of the uraninite crystal, the total reaction may be expressed as follows:



The significance of this reaction is easy to understand from the diagram (figure 1), which

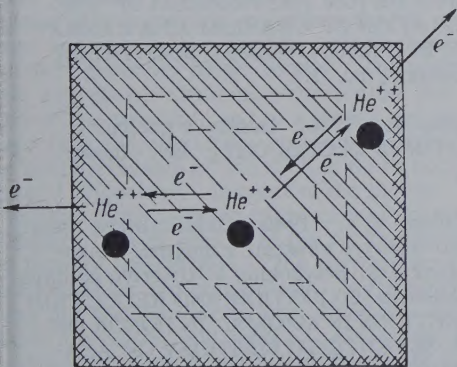


FIGURE 1. Diagram showing the possible transformations of  $\alpha$ -radiation ( $\text{He}^{++}$ ) into He at the expense of  $\beta$ -radiation ( $e^-$ ) in the central and peripheral parts of a uraninite crystal. The frequency of the hatch-marks tentatively indicates the zonality of this phenomenon; the black circles are the decaying atoms of uranium.

shows that only inside the crystal is the  $\text{He}^{++}$  transformed into uncharged He atoms by drawing electrons from the atomic nuclei of the radioactive elements. In the outer zone, extending to a depth of several hundredths of a millimeter, from below which no  $\text{He}^{++}$  ions can emerge, and further to the depth of 0.3 - 0.5 cm, from below which no  $e^-$  can emerge, the uraninite crystal will lose some part of its electrons and al-

most all its  $\gamma$ -particles.

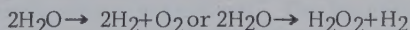
If this is so, one may readily understand that the  $\text{He}^{++}$  ions expelled from the nuclei without being compensated by electrons will be transformed into He atoms mainly by drawing electrons from oxygen ions, which are numerically predominant in the compound and contain four electrons with ionization potentials smaller than the second ionization potential of He. As a result, the  $\text{O}^{2-}$  ions become  $\text{O}^{\downarrow\downarrow}$  atoms. But since the latter have a great tendency to enter into chemical bonds, they will soon react with  $\text{U}^{4+}$  to form  $\text{UO}_2^{++}$  ions.<sup>6</sup> Because of this process, the external zones of uraninite crystals acquire a positive charge.

The surface layers of uraninite crystals may regain their electrical neutrality, either by a subsequent loss of  $\text{UO}_2^{++}$ , or by adsorbing  $\text{O}^{2-}$  ions from the surrounding medium. Under certain particular conditions, this may also take place by the loss of  $\text{Pb}^{++}$ .

Nature, apparently, follows the first and second courses. The leaching action of aqueous solution is required to bring about a loss of  $\text{UO}_2^{++}$ . Komlev (1957) has observed this action in pegmatites taking place almost to the complete loss of all the uraninite. The adsorption of  $\text{O}^{2-}$  ions may occur through two processes. The more usual is probably dissociation of water, which readily penetrates the surface layers of the crystals, into  $\text{O}^{2-}$  and  $\text{H}_2$ ; this ultimately takes place through the reducing action upon  $\text{H}^+$  of electrons emanating from the uranium nuclei. There may also be a dissociation of the silicates surrounding the uraninite by a similar action of the same electrons on the cations.

When  $\text{H}_2\text{S}$  is present in the solution, there may also be a loss of  $\text{Pb}^{++}$ , and sometimes even  $\text{S}^{2-}$  ions (along with the  $\text{O}^{2-}$ ) may be drawn into the crystal in the formation of tiny segregations of galena within the uraninite. In this process some part (though probably a small one, because of their brief lives) may be played by the loss of  $\text{Ra}^{++}$  and Rn.

It must be noted that the possibility of a dissociation of water with a subsequent loss of  $\text{H}_2$ , resulting from radiochemical processes, has long been used as an explanation for the secondary or supplementary oxidation of uraninite (Khlopin, 1938), but this dissociation has been envisaged only as the reaction:

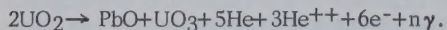


<sup>6</sup> It may be noted in passing that the chemical bonds in  $\text{UO}_2^{++}$  are not fully ionic, and that this ion probably contains not  $\text{U}^{6+}$  and  $\text{O}^{2-}$ , but rather  $\text{U}^{\downarrow\downarrow\downarrow\downarrow\downarrow}$  and  $\text{O}^{\downarrow}$  (Lebedev, 1957), following the formula  $\text{O}^{\downarrow}-\text{U}^{4+}-\text{O}^{\downarrow}$ .



From what has been said above it is clear that the process of "subsequent oxidation" is not always the result of an increase in the oxygen potential in secondary, superimposed processes, but rather more profound or fuller manifestation of the phenomenon of auto-oxidation proper, occurring rather in the outer zones of uraninite crystals owing to the different penetrating capabilities of  $\alpha$ - and  $\beta$ -radiation and to the possible discharge of  $\beta$ -radiation. If this is the case, then the smaller the uraninite crystal, the more completely its  $\text{UO}_2$  will be altered to  $\text{UO}_3$ . This transformation will undoubtedly be affected by the surrounding medium: the presence or absence of water, the possibility of a reverse (ultimately) return of electrons (by means of internal conversion, for example), the form in which the uraninite has accumulated and a number of other circumstances. As regards uranium oxidation that is actually secondary, there is no doubt that this also takes place. This process is especially characteristic of hypergenesis (Komlev, 1957). The superimposed processes, however, may also involve partial reduction (of  $\text{UO}_3$  to  $\text{UO}_2$ ). This is evidently the means by which penetrating solutions have formed martite aureoles around uraninite inclusions in magnetite (Soboleva and Pudovkina, 1957). A comparison of the oxidation-reduction potentials of the reactions with the formation of  $\text{UO}_3$  and  $\text{Fe}_2\text{O}_3$  testifies to this very possibility.

Thus in the oxidation of uranium in uraninites, in addition to the usual and well known process of auto-oxidation according to the Kirsch-Khlopina reaction, which holds true for the interior of the crystals, in the surface zones of uraninite crystals and segregations there is a still more intensive auto-oxidation resulting from a loss of some part of the electrons radiating from the nuclei of the radioactive elements formed in the decay of uranium, in accordance with the overall reaction:



The positive charge on the uraninite crystals produced by this reaction, which transforms each of them into a peculiar sort of anode, along with a number of radiochemical reactions such as dissociation of water, is probably the main reason for the formation of the intensively oxidized outer zones of uraninite crystals. In certain cases there are also secondary process of oxidation, and sometimes, possibly, partial reduction (of  $\text{UO}_3$  to  $\text{UO}_2$ ).

## REFERENCES

- Khlopina, V. G., 1938, Kislorodnyy method opredeleniya geologicheskogo vozrasta po atomnomu raspadu i yego primeneniye k opredeleniyu vozrasta Karelskikh uraninitov i uranitov iz Vilberforsa i Yuzhnoy Dakoty [THE OXYGEN METHOD OF DETERMINING GEOLOGIC AGE BY RADIOACTIVE DECAY AND ITS APPLICATION IN DETERMINING THE AGES OF THE KARELIAN URANINITES AND THE URANINITES FROM WILBERFORCE AND SOUTH DAKOTA]: *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya*, no. 2.
- Komlev, L. V., 1957, K geokhimii radioaktivnykh elementov v pegmatitovom pole severnoy Karelii v svyazi s voprosom vozrasta Belomorskikh intruziy [ON THE GEOCHEMISTRY OF THE RADIOACTIVE ELEMENTS IN THE PEGMATITE FIELD OF NORTHERN KARELIA IN RELATION TO THE PROBLEM OF THE AGE OF THE WHITE SEA INTRUSIVES]: *Tr. Radiyev. Inst. im. V.G. Khlopina Akademii Nauk SSSR*, v. 5, no. 2.
- Lebedev, V. E., 1957, Osnovy energeticheskogo analiza geokhimicheskikh protsessov [PRINCIPLES OF ANALYSIS OF THE ENERGY INVOLVED IN GEOCHEMICAL PROCESSES]: *Izd. Leningrad. Univ.*
- Leonova, V. A., 1959, K mineralogii i kristalloghimii uraninitov Severnoy Karelii [ON THE MINERALOGY AND CRYSTAL CHEMISTRY OF THE URANINITES OF NORTHERN KARELIA]: *Zap. Vsesoyuzn. Miner. Obshch.*, ch. 88, no. 1.
- Naumov, G. B., 1959, K voprosu o karbonatnoy forme perenosy urana v gidrotermalnykh rastvorakh [ON THE PROBLEM OF THE MIGRATION OF URANIUM AS A CARBONATE IN HYDROTHERMAL SOLUTIONS]: *Geokhim.*, no. 1.
- Rankama, K., 1956, Izotopy v geologii [ISOTOPES IN GEOLOGY]: *Izd. Inostr. Lit.*
- Shcherbina, V. V., 1946, Okislitelnyye i vostanovitelnyye reaktsii v magme. Akademiku D. S. Belyankinu k 70-letiyu so dnya rozhdeniya [OXIDATION AND REDUCTION REACTIONS IN MAGMA: IN HONOR OF THE SEVENTIETH BIRTHDAY OF ACADEMICIAN D. S. BELYANKIN]: *Sb. Akademii Nauk SSSR*.
- Shchukarev, S. A., 1954, O periodichnosti svoystv elektronnykh obolochek [ON THE PERIODIC NATURE OF THE PROPERTIES OF ELECTRON SHELLS]: *Vestnik LGU*, no. 11.
- SIDORENKO, G. A., 1958, Rentgenograficheskoye izucheniye prirodnnykh okislov urana [AN X-RAY STUDY OF NATURAL OXIDES OF URANIUM]: *Geokhim.*, no. 1.
- Soboleva, M. V. and Pudovkina, I. A., 1957, Mineraly urana. Spravochnik [URANIUM MINERALS: A REFERENCE GUIDE]: *Gosgeoltekhizdat*.



# THE ENTRY OF URANIUM INTO SOME ROCK-FORMING MINERALS<sup>1</sup>

by

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• translated by Michael Fleischer •

## ABSTRACT

Samples of three Tien Shan granites were analyzed for the U content of their constituent minerals. Three minerals with high U content are allanite (450-500 ppm), monazite (1,000-1,300 ppm) and zircon (1,600-1,860 ppm), but significant amounts, from 20 to 40 ppm occur in the biotite, muscovite, amphibole, apatite, ilmenite, sphene, and chlorite. From 30 to 60 percent of the total U in the granites could be leached from the minerals. The unleachable portion of U may enter the crystal lattices of minerals by isomorphism or endocryptism. --M. Russell.

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During the study of the old granitic rocks of the Tien-Shan, we established that there were increased contents of uranium in some rock-forming minerals: amphibole, biotite, muscovite, apatite, chlorite, and some others.

The granitic rocks here are diverse in outward aspect and petrographic characteristics. They may be separated into several varieties, connected by gradual transitions from normal biotite granites and granites enriched in feldspar minerals to granodiorites, quartz diorites, and quartz monzonites.

The most abundant is a series of biotite granites with rare hornblende, mostly porphyritic, medium-, and irregular-grained. They consist of transparent, colorless quartz, microcline and microcline-perthite, plagioclase, and dark greenish-brown biotite. The porphyritic segregates are mainly microcline and microcline-perthite, and to a lesser degree plagioclase and oligoclase-andesine. Around the porphyroblasts of microcline there occur rims of oligoclase. In most of the biotite granites, there is more plagioclase than alkali feldspar. Biotite occurs in the rocks mainly in the form of intergrowth in the porphyritic segregated feldspar and plagioclase. In the biotite there are frequent inclusions of zircon, apatite, titanomagnetite, and sphene. Around the inclusions of zircon in the biotite there are found intense pleochroic halos. Together with the biotite there occurs hornblende in small amount. Biotite and hornblende are sometimes chloritized. The accessory minerals in the biotite granites are apatite, zircon, titanomagnetite, sphene, allanite, monazite, xenotime, and thorite.

The biotite granites are connected by gradual transitions to biotite-hornblende granites, which, to the degree of increase of their content in plagioclase go through a transition into plagioclase granites, approximating granodiorites or quartz monzonites. In some varieties of porphyritic biotite-hornblende microcline-perthite granites, the usual hornblende is replaced by alkali hornblende. Of the accessory minerals in the plagioclase-bearing granites, the main role is played by sphene and allanite. Fluorite occurs in these granites. The grains of fluorite are enclosed in the main part of the granite and often, together with chlorite, are located along veins. In the fissures with the fluorite are associated topaz, tourmaline, and lithium micas. The granodiorites are enriched in oligoclase and oligoclase-andesine, which are strongly sericitized and saussuritized. Biotite and hornblende are intensely chloritized. Quartz is present in large amounts, but always occupies the interstices between crystals of plagioclase. K-Na feldspars are generally absent in the granodiorite.

The quartz monzonites are the marginal facies of the granitic intrusives or form schlieren in the granites. They consist of large grains of quartz and grids of microcline, which are crowded with inclusions of andesine and hornblende. Hornblende and biotite are often intergrown with one another. Of the accessory minerals in the monzonite, apatite is conspicuously more common than in the granites. Zircon and sphene are present in small amounts, as in the granites. The biotite-hornblende and hornblende-biotite quartz diorite form marginal facies of the granitic intrusives. According to outward aspect these are greenish-gray dark gneissic rocks. The plagioclase in them is andesine and is nearly always sericitized. The hornblende, commonly or rarely alkali, occurs intergrown with biotite. In the hornblende and biotite are many inclusions of zircon, apatite, sphene, and titanomagnetite. Around the zircon grains are developed intense pleochroic aureoles.

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Many massifs of the granitic rocks have indications of increased alkalinity. Magmatogenic



uranium minerals rarely occur in the igneous rocks of the region; they are concentrated in pegmatites, and in pneumatolytic and hydrothermal formations. In the granitic rocks, their dike derivatives and pegmatites are notably abundant in accessory and secondary minerals in which uranium is an important constituent part. Increased concentrations of uranium are noted in thorianite, thorite, allanite, zircon, monazite, xenotime, tantaloniobates, and other minerals.

In distinction from thorium, uranium is more associated with mineralizers and hydrothermal solutions. The association of uranium with magmatic solutions leads to its concentration in pegmatitic and hydrothermal formations, but this association is also one of the factors of the dissemination of uranium with the capillary hydrothermal solutions that remain in the rocks and the disseminated minerals which are formed from these solutions.

Lump samples from various parts of the massif of the biotite granite region showed contents of uranium from 3.5 to 8.5 ppm, hornblende-biotite granites from 3.8 to 8.7 ppm, marginal facies of the massif of biotite granite from 6.0 to 10.5 ppm.

By comparison with the more abundant biotite granite, notably higher contents of uranium are shown by individual stocks and dikes of alkalic microcline granites.

To study the radioactivity, fractions of the rock-forming minerals were studied.

In the analyzed samples of granite, more than one-third of the uranium is present in the fractions of accessory minerals, in which it is contained in increased concentrations. Up to one-third of the total amount of uranium in the samples is in the fraction of the femic rock-forming minerals, in which uranium is concentrated several-fold over its content in the rock, and less than one-third is in the feldspar and quartz, in which the concentration of uranium is significantly lower than the average content in the rock (table 1).

TABLE 1. Content of uranium in granites and minerals separated from granites

Mineral	Content of Uranium, ppm		
	1*	2*	3*
Quartz	2.1	3.0	2.5
Microcline	3.1	3.5	3.8
Plagioclase	4.2	3.8	4.4
Biotite	40	26	32
Muscovite	20	--	18
Amphibole	35	28	30
Apatite	32	25	30
Allanite	500	600	450
Zircon	1,860	1,600	1,760
Monazite	1,300	1,200	1,000
Ilmenite	40	30	35
Sphene	35	30	40
Chlorite	20	15	15
In the rock	8.2	7.7	7.6

1\* - Biotite granite. 2\* - Biotite-amphibole granite. 3\* - Biotite granite.

The plagioclase feldspars of the analyzed granites are oligoclase and oligoclase-andesine. The amphibole is the common brown hornblende, somewhat enriched in sodium. In the hornblende and biotite there is scandium in amounts from 0.003 to 0.006 percent.

Under the action of hydrochloric acid on finely powdered granite on heating, 30 to 60 percent of the total content of uranium is leached from the sampled rocks. Thereby only a very small amount of rock is dissolved. Significant amounts of uranium are leached also from the granite by a 2-5 percent solution of sodium carbonate.

Samples of rock-forming minerals, taken for the leaching of the uranium, were purified with difficulty from admixtures and were free from inclusions of other minerals visible under the binocular microscope. The minerals were ground to 0.02 mm and in amounts of 2-5 g were boiled with 50 ml 2N hydrochloric acid for one hour. Thereby there dissolved only a small amount of the samples, while the amount of uranium leached attained 50 percent and more of its initial content in the mineral fraction. Further leaching of the uranium proceeded very slowly, parallel to the solubility of the rock-forming minerals. The results of the experiments are given in Table 2.

TABLE 2. Amount of leachable uranium from rock-forming minerals of granites

Mineral	Content of uranium ppm	Percent of leachable uranium	Content of uranium in residue ppm	Percent of mineral dissolved
Quartz	2.1	48	1.0	0.5
Microcline	3.1	55	1.5	1.0
Plagioclase	4.2	52	2.0	1.3
Hornblende	35.0	32	28.0	3.2
Biotite	40.0	26	33.0	4.5
Muscovite	20.0	35	16.0	4.1

[Tr. Note: The percent U leached would seem to be 20 percent for hornblende, 17.5 percent for biotite, 20 percent for muscovite. --M. F.].



Uranium, leachable from the rock-forming minerals without decomposition of their crystal lattices, may belong to some soluble accessory minerals of uranium, which may occur in the form of visible inclusions and as the first pigment impossible to find in the dispersed state. A significant part of the uranium leachable from the rock-forming minerals without notable solution of them may come from compounds which are formed from hydrothermal solutions which saturated the granites in the final stages of their formation. Uranium goes into the solution, which may occur in the endogenic pores and intergranular solutions and in the liquid inclusions inside the minerals, in the formed exogenic emanations, and in the highest dispersions -- microscopic disseminations in the rocks and minerals (according to V. I. Vernadsky, 1934). Notable amounts of uranium may be leached in connection with the corrosion and partial solution of uranium-containing rock-forming minerals: hornblende, biotite, etc. The lowest contents of leachable uranium are found in quartz and feldspars. Significantly greater concentrations were determined in amphiboles, micas, chlorites, and apatites.

Of the pure grains of hornblende and mica after their treatment with acid, thin sections were prepared without a glass cover. Micro-radiography of sections of grains of hornblende, biotite, muscovite and chlorite, and apatite, free or as inclusions foreign to the mineral, showed a uniform distribution of tracks of alpha-particles in the photolayer under the entire layer of the crystals. In them there were not found centers of concentration of tracks of alpha-particles, which are characteristic for the micro-radiography of crystals containing microscopic inclusions of zircon, monazite, and other radioactive minerals. Microchemical analyses taken from sections of grains of hornblende, biotite, muscovite, apatite, free or inclusions, gave from 10 to 60 ppm uranium. The hornblende and biotite from marginal parts of the granite massifs, stocks of alkali granites, and dikes of granite are more enriched in uranium than the same minerals from granodiorites, quartz monzonites, and porphyritic granites of the inner parts of the intrusives. Some free or included crystals of hornblende and biotite from the peripheral parts of alkali granites and from their granite dikes contain up to 0.02 percent unleachable uranium.

Biotite in aplite-pegmatitic veins of granites consist of two generations. The earlier generation of biotite is developed in salbands in the far-contact parts of the veins in fine-grained quartz-feldspar masses. The later generation developed in the pegmatitic -- interior coarse-grained -- parts of the vein. Biotite of the earlier generation from aplitic borders of the vein contains from 30 to 60 ppm; biotite from pegmatitic parts of the vein from 5 to 30 ppm uranium. Some crystals of biotite from the pegmatitic parts of the

vein show higher contents of uranium in the inner zones of the crystals than in the outer zones. Here, apparently, there is present the phenomenon of self-purification -- autolysis -- in the process of growth of the crystals of biotite.

The uranium not leachable from the rock-forming minerals -- hornblende, mica, etc., may belong to the insoluble compounds of uranium included in them in a state of dispersion impossible to detect optically or to soluble compounds of uranium, hidden in the minerals and not accessible to the action of the solvent.

The unleachable uranium may enter in the rock-forming minerals in connection with local heterogeneities and defects, possible in their structure. Uranium may enter isomorphously into the crystal lattices of hornblende, mica, chlorite, apatite, and many other rock-forming minerals, in which the atoms (ions) of uranium may occur in the state of entrapment -- endocryptism. This regular entrainment of uranium ions in the crystal lattice of many minerals is connected with its crystallochemical properties. In the endocryptic isomorphism of the leading elements that build the lattice, there are entrained atoms and ions of the minor elements similar to them, often concentrating them from melts or solutions, in which their content is low. During the processes of endocryptism there arise also both isovalent and heterovalent replacements, with observance of the rules of crystallochemical compensation.

A. E. Fersman showed that there are no sharp boundaries between isomorphism and endocryptism. "The differences between these phenomena are rather quantitative; in the case of isomorphism we are dealing with two more or less equivalent elements, of which both may form their own lattices, whereas in the phenomena of endocryptism we always differentiate the leading element and the subordinate, minor one" (Fersman, 1955).

In some rock-forming minerals uranium is associated with very complex compounds, in the formation of which mineralizers --  $\text{OH}^-$ ,  $\text{F}^-$ ,  $\text{H}_2\text{O}$  -- take part.

The entry of uranium into the crystal lattice of amphibole, mica, some chlorites, and the structures of minerals analogous in composition may be accomplished by the replacement of  $\text{Ca}^{2+}$ ,  $(\text{Fe}^{2+}, \text{Mg}^{2+})$  by  $\text{U}^{4+}$  with parallel replacement of  $(\text{OH})^{1-}$  and  $\text{F}^{1-}$  by  $\text{O}^{2-}$ , and for yttrium and rare earths, according to the scheme  $\text{Ca}^{2+}$  by  $\text{Y}^{3+}$  with simultaneous replacement of  $\text{OH}^{1-}$  by  $\text{O}^{2-}$ . Similar heterovalent isomorphism is known in allanite, apatite, fluorite, and many other minerals, where  $\text{Ca}^{2+}$  is replaced by  $\text{Ce}^{3+}$ ,  $\text{Y}^{3+}$ ,  $\text{Th}^{4+}$ , and  $\text{U}^{4+}$ , with parallel replacement of  $(\text{F}, \text{OH})^{1-}$  by  $\text{O}^{2-}$  and  $2(\text{F}, \text{OH})^{1-}$  by  $2 \text{O}^{2-}$ . There are other possible schemes of the endocryptic entry of uranium into rock-

forming minerals. In muscovite one may assume the endocryptic replacement of  $\text{Al}^{3+}$  in octahedral coordination by  $\text{U}^{4+}$  and the parallel one of  $(\text{OH})^{1-}$  by  $\text{O}^{2-}$  or of  $\text{Si}^{4+}$  by  $\text{Al}^{3+}$  (! M.F.).

In apatite there occurs the endocryptic replacement of  $\text{Ca}^{2+}$  by  $\text{U}^{4+}$  with the simultaneous replacement of  $2(\text{F}, \text{OH})^{1-}$  by  $\text{O}^{2-}$ . In apatite is also possible the replacement of  $\text{Ca}^{2+}$  by  $\text{U}^{4+}$  with the simultaneous replacements  $\text{P}^{5+}$  by  $\text{C}^{4+}$  and  $(\text{F}, \text{OH})^{1-}$  by  $\text{O}^{2-}$ , or  $2\text{P}^{5+}$  by  $2\text{C}^{4+}$ , and  $\text{P}^{5+}$  by  $\text{C}^{4+}$  with simultaneous replacement  $\text{O}^{2-}$  by  $(\text{F}, \text{OH})^{1-}$ , i.e.  $(\text{PO}_4)^{3-}$  by  $\text{CO}_3$ ,  $(\text{F}, \text{OH})^{3-}$ . Other schemes of the endocryptic entry of uranium into apatite are possible.

Besides the many minerals of thorium zirconium, rare earths, niobium and titanium -- which are leading in comparison with uranium, and entraining it into the lattices of their minerals -- there may be rock-forming calcium-iron, calcium-magnesium-iron, and to a lesser degree calcium-aluminum silicates.

One of the leading petrogenetic elements with respect to uranium is calcium, the role of which is very significant in magmatic and sedimentary rocks. Important roles may also be assumed by iron and by other elements.

Uranium takes part widely in isovalent and heterovalent isomorphism in very many minerals and thereby to a significant degree is dispersed in rocks.

Thanks to the high sensitivity and the accuracy of the methods of study at present, one can determine the content of uranium in material to  $10^{10}$ - percent. As for many other elements, numerous studies have confirmed the ideas of V. I. Vernadsky and A. E. Fersman relative to the dispersion of atoms of uranium.

Analyses of rock-forming minerals from granitic rocks often show notable contents of uranium in pyroxenes, amphiboles, micas, chlorites, zeolites, epidotes, zoisites, tourmalines, garnets, apatites, cancrinites, feldspars, fluorites, and many other minerals. Chlorites, micas, apatites, and fluorites from the contact zones of some hydrothermal uranium deposits contain increased concentrations of uranium. Uranium in the minerals enumerated may occur in the form of endocryptic admixture. The manifestation of endocryptism, like sorption, encompasses a wider group and a series of elements and their compounds than does isomorphism, especially in connection with the fact that endocryptic elements enter only in small amount into the crystal structures of compounds of leading elements and do not disturb

their crystal-chemical equilibrium. The rules of endocryptism are all in the first place determined by closeness of size and similarity of properties of atoms and ions, but they may be less bounded by similarity and closeness of the ions picked up then in cases of complete or incomplete inter-replacements of atoms in isomorphous admixtures, or often depend more on the reactive mass of the element. But here, in the phenomena of self-purification and autolysis, as in selective sorption, there appear general tendencies of differentiation of matter according to similarities of atoms and ions.

Some authors state that uranium in magmatic and hydrothermal solutions, as in exogenic solutions, migrates in the sexivalent form and is reduced to the quadrivalent only during mineral formation in ore fields. The entry of uranium into accessory and rock-forming minerals shows that its entry into magmatic solutions is also in the quadrivalent form.

The occurrence of uranium in the sexivalent form ought to limit its entry into the lattices of rock-forming minerals and to contribute to its accumulation in the residual solutions.

Endocryptism, like sorption, is one of the important factors of migration, dissemination, and concentration of uranium in endogenic and exogenic formations. For dispersed mineral formation, which is especially widely developed in soils and sedimentary deposits, sorption endocryptic forms of accumulation of uranium and other rare elements are characteristic.

## REFERENCES

- Belov, N. V., 1939, [ON ISOMORPHIC REPLACEMENTS IN THE APATITE GROUP]: Doklady Akad Nauk SSSR, v. 22, no. 2.
- Borneman-Starynkevich, I. D., 1938, [SOME ISOMORPHOUS REPLACEMENTS IN APATITE]: Doklady Akad Nauk SSSR, v. 19, no. 4.
- Borneman-Starynkevich, I. D., and Belov, N. V., 1940, [ISOMORPHOUS REPLACEMENTS IN CARBONATE-APATITE]: Doklady Akad Nauk SSSR, v. 26, no. 8.
- Fersman, A. E., 1955, Geokhimii, v. 1-2 Izbr. Trudy, t. 3, Izd. Akad Nauk SSSR.
- Larsen, E. S., Phair, G., Gottfried, D., and Smith, W. L., 1956, [URANIUM IN MAGMATIC DIFFERENTIATION. GEOLOGY OF ATOMIC RAW MATERIALS]: INGI.
- Saukov, A. A., 1950, Geokhimii. Gosgeolizdat.
- Vernadsky, V. I., 1934, OUTLINE OF GEO-CHEMISTRY (4th ed., 2nd Russian): ONGI.



# THE GEOCHEMISTRY OF TANTALUM AND NIOBIUM<sup>1</sup>

by

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• translated by Michael Fleischer •

## ABSTRACT

Ta and Nb are associated in nature. Both are oxyphile and are related geochemically to Fe, Mn, U, rare earths U, Th, Zr, W, Sn, Bi, and Sb. Both accompany the alkali metals, especially Na and Li. Their close relationship explains their isomorphism in mineral-forming processes. Zr, Sn, and Nb entrain Ta and Nb in the crystal lattices of their minerals in limited amounts. The concentration of Ta and Nb increases in the course of magma evolution from ultrabasic to alkalic. Nb predominates over Ta in the main kinds of rocks by from 5:1 to 17:1. Only in granite pegmatites is Ta dominant. In granitic rocks Ta and Nb are associated with Fe, Mn, Bi, Sb, W, and Sn. In granosyenitic complexes they form complex minerals with Ti, rare earths of the Y subgroup, U, and Th. Concentrations of Ta and Nb in granitic and granosyenitic complexes increase toward the end of the magmatic and pegmatitic processes, and afterward diminish toward the end of the pneumatolytic-hydrothermal processes. In alkalic complexes Ta and Nb are associated with Ti, rare earths of the Ce group, and Th. Concentrations of Ta and Nb in alkalic massifs are caused by magmatic differentiation. In alkalic ultrabasic complexes, in magmatic and pegmatitic processes, Ta and Nb do not form independent minerals but enter into minerals of Ti and Fe, i.e. perovskite, titanomagnitite, and pyroxenes. --M. Russell.

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## INTRODUCTION

Tantalum and niobium have similar physical, chemical, and crystallochemical properties and therefore accompany one another in natural processes. Both these elements are in the second subgroup of the fifth group of elements of the periodic system of Mendeleev, are characterized by uneven atomic number, similar size of ionic radii, and in natural compounds occur in the quinquivalent form.

Studies of the abundances of tantalum and niobium in the earth's crust, meteorites, and various minerals began at the end of the 19th century, but up to the present these problems are far from solution, which is explained in

the first place by the difficulty of the determination of small amounts of these elements and their separation from one another.

## ABUNDANCES OF TANTALUM AND NIOBIUM IN THE EARTH'S CRUST

Calculation of the clarkes of tantalum and niobium in the earth's crust has interested both foreign and Soviet scientists, but the values obtained by different investigators diverge to a considerable degree (table 1).

The most reliable is the clark of Rankama, based on 76 direct chemical determinations of tantalum and niobium in various igneous rocks.

TABLE 1. Weight clarkes of Ta and Nb in the earth's crust in parts per million

Year	Author	Nb	Ta	Nb/Ta
1898	Fogg	0.00n	0.00n	-
1924	Clarke and Washington*	0.000n	30	-
1924	V. I. Vernadsky	-	1-10	-
1923-1928	A. E. Fersman	0.32	-	-
1927	Behrendt and Berg	-	0.012	-
1930	V. I. Vernadsky	0. n	1	-
1929-1932	Hevesy	0.32	0.24	1.3
1932	Berg	0.6	0.2	3
1937	V. M. Goldschmidt*	20.	15.	1.3
1947	Rankama*	24.	2.1	11.4
1949	A. P. Vinogradov	10.	2.	5.

Note: Given in percent in Russian original.  
For igneous rocks.

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TABLE 2. Average contents of niobium and tantalum in various igneous rocks in parts per million

Rock	After V. M. Goldschmidt (1933)	After A. P. Vinogradov (1956)		After K. Rankama (1944, 1947)		
	Nb	Nb	Ta	Nb	Ta	Nb/Ta
Monomineralic ultra-basic	-	-	-	0.3	0.7	0.4
Ultrabasic	-	15.	0.75	16.	1	16
Eclogites	-	-	-	3	0.7	4.3
Gabbro	8.	20.	1	19	1.1	17.3
Diorites	24.	3.5	0.7	3.6	0.7	5.1
Granites	40.	20.	3.5	21	4.2	5.0
Syenites	-	-	-	30	2	15
Nepheline syenites	160.	-	-	310	0.8	387.5
Alkalic ultrabasics	-	-	-	14	1.2	8.3

Note: Given in percent in Russian original.

These data showed that niobium is much more abundant in nature than tantalum.

The contents of tantalum and niobium in various types of rocks vary within wide limits (table 2).

The numbers given indicate that the content of the sums of niobium and tantalum in igneous rocks in general increase from the ultrabasic rocks to the acid and the alkalic. Nevertheless, these numbers are lacking in verification and precision, because they are based on an insufficient number of analyses. In particular, the predominance of tantalum over niobium in monomineralic ultrabasic rocks causes doubts. Also not clear are the low contents of niobium and tantalum in diorites, as compared with gabbros. The data of K. Rankama and A. P. Vinogradov as to the contents of tantalum and niobium in granites are reliable, but also deserve verification.

In the granites of Kalby, according to the data of E. B. Znamensky (1957), the content of niobium varies from 10 to 21 ppm, and of tantalum from 1.3 to 2.2 ppm.

Studies by the author of biotite granites of Central Kazakhstan showed that the content in them of Nb (average of 6 analyses) is 27 ppm and of Ta (in one sample) 8 ppm.

Studies of nepheline syenites made by L. S. Borodin (1955) on the Khibina massif, by V. I. Gerasimovsky (1955) (given as 1937) on the Lovozero massif, and by E. M. Eskova and I. P. Tikhonenkov on other alkalic massifs showed that the contents of niobium and tantalum are highly variable (table 3); the average contents of niobium and tantalum in nepheline syenites, calculated by Rankama on the basis of only two chemical analyses, absolutely cause doubts.

The contents of  $Ta_2O_5$  in sedimentary rocks, according to the data of K. Rankama, are as follows: In individual samples of bauxite

5-7 ppm, kaolin 100, Dictyonema shale 2, clayey shale 4, gas coal 0.07, shungite 0.1, glacial clays 2, and recent clay 20 ppm. The average contents of  $Nb_2O_5$  in sedimentary deposits and the ratio of Nb/Ta are given in Table 4.

The numbers given indicate that the highest concentration of tantalum and niobium, in a series of cases exceeding the clarkes, are found in the deep-water oceanic sediments.

#### SYSTEMATICS OF MINERALOGY OF TANTALUM AND NIOBIUM AND FEATURES OF THEIR ISOMORPHOUS ENTRY INTO THE CRYSTAL LATTICES OF MINERALS

The closeness of the sizes of the ionic radii, and also of the chemical properties of tantalum and niobium explain the simultaneous entry of these two elements in one and the same minerals. In fact, there are no tantalum minerals that do not contain niobium, and no niobium minerals that do not contain tantalum. Tantalum and niobium, together with Fe, Mn, Ti, Zr, rare earths, U, Th, Sb, Bi, and Sn form complex minerals, in the crystal lattices of which they enter entirely in six-fold coordination.

At present 72 minerals are known (counting varieties) of tantalum and niobium (table 5). All these minerals, in accord with the universal classification of Dana, belong to two classes of natural compounds, oxides and silicates, most belonging to the class of oxides of families  $R_2O_3$  and  $RO_2$  (Strunz, 1957). Most of the minerals have very complex chemical compositions, in consequence of the entry into them of various elements: Nb, Ta, Ti, Zr, Fe, Mn, Mg, Ca, Na, Y, Ce, La, U, Th, Si, Al, Sb, Bi, Sn, and others, which makes it difficult to write the formula. This impelled the author to systematize the minerals of tantalum and niobium according to their types of chemical formulas. For simplification of the chemical



TABLE 3. Contents of Ta and Nb (ppm) in nepheline syenites

Rock	(Ta, Nb) <sub>2</sub> O <sub>5</sub>	Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Author
garnites, Khibina massif	200	-	-	L. S. Borodin (1955)
garnites, Khibina massif	80	-	-	L. S. Borodin (1955)
garnites, Khibina massif	80	-	-	L. S. Borodin (1955)
garnites, Khibina massif	300	-	-	L. S. Borodin (1955)
garnites, Lovozero massif	560	520	40	V. I. Gerasimovsky (1957)
garnite-lujavrite, Lovozero massif	1,008	940	68	V. I. Gerasimovsky (1957)
nepheline syenites, Tatarki Mt., Yenisey Ridge	200	-	-	Data of I. P. Tikhonenkov
nepheline syenites, Kii Mt., Yenisey Ridge	150	-	-	Data of I. P. Tikhonenkov
garnite-urtite, Kii Mt., Yenisey Ridge	670	-	-	Data of I. P. Tikhonenkov

TABLE 4. Average contents of niobium (ppm) in sedimentary rocks, after Rankama (1947)

Sediment	Nb <sub>2</sub> O <sub>5</sub> , ppm	Nb/Ta
basaltic	18	9.0
chemical	0.6	2.6
granogenic	0.9	3.8
deep-water oceanic	59	41.9

formula, all the cations entering into these minerals are divided into three groups, according to the principles of G. B. Boky (1956), with calculation of their crystallochemical roles.

To the first group (A) are referred the chemical elements with large ionic radius ( $>0.80\text{\AA}$ ), entering into the crystallochemical lattices of minerals predominantly with 8-fold or higher coordination (rarely in six): Na, Ca, La, Y, Th, U, Bi<sup>3+</sup>, Sn<sup>2+</sup>, Fe<sup>2+</sup>, Mn<sup>2+</sup>. To the second group (B), are referred elements with ionic radii from 0.57 to 0.80 $\text{\AA}$ , entering into crystal lattices of the minerals predominantly in six-fold coordination: Nb, Ta, Ti, Mg, Fe<sup>3+</sup>, Al, Sn<sup>4+</sup>, Bi<sup>5+</sup>, Sb<sup>5+</sup>. The third group ("Si") unite the metalloids: Si, P, and Al, i.e. elements with sizes of ionic radii lower than 0.57 $\text{\AA}$ , entering into the crystal lattice of the minerals in 4-coordination.

As anions ("X") of the minerals of tantalum and niobium, besides oxygen, there are often hydroxyl group, fluorine, and chlorine.

In Table 5 are given the systematics of the minerals of tantalum and niobium according to the types of their chemical formulas, showing their abundance in the rocks and vein formations of various magmatic complexes. These systematics are preliminary, because the chemical composition of a series of minerals has as yet studied insufficiently and their chemical formulas are calculated approximately. The most poorly studied are the titano-niobates of the rare earths, uranium, and thorium, having the most complex chemical compositions.

As seen from Table 5, the largest number of minerals of tantalum and niobium occur in rocks and vein derivatives of granitic and granosyenitic complexes, although the largest deposits of these elements are genetically associated with nepheline syenites and alkalic ultrabasic rocks. In genetic association with medium, basic, and ultrabasic rocks of the alkali-earth series, minerals of tantalum and niobium are practically not found. Independent tantalum minerals in which tantalum predominates over niobium are found solely in granites, rarely in granosyenite pegmatites and are not found in association with alkalic nepheline syenites and alkalic ultrabasic rocks. For the granitic and granosyenitic complex rocks and their vein and metasomatic formations are characteristic minerals of the columbite-tantalite group and microlite, and also the complex-tantalo- and titano-niobates of the rare earth yttrium subgroup and uranium. The alkalic rocks are characterized by minerals of the perovskite group and pyrochlore, complex titano-niobates of the rare earths of the cerium subgroup and thorium, and also silicates of titanium and niobium.

In minerals of tantalum and niobium there is found both isovalent and heterovalent isomorphism. Isovalent isomorphism is found between tantalum and niobium. The closeness of the ionic radii (0.66 for Nb<sup>5+</sup> and Ta<sup>5+</sup>) explains not only their occurrence together, but also the two-way isomorphism with zirconium in many materials. The clearest isomorphism of tantalum and niobium is expressed in minerals of the tantalite-columbite group, in which both the tantalum and niobium end members and intermediate varieties are known. Great variation in the contents of tantalum and niobium is also observed in the minerals of the groups moscovite-tapiolite, pyrochlore-microlite, euxenite-polycrase, samarskite, fergusonite, and beta-fite.

Heterovalent isomorphism in minerals of tantalum and niobium is widely developed among niobium, tantalum, and titanium, which is explained by the closeness in size of the

TABLE 5. Systematics of minerals of tantalum and niobium

Type of For- mula	Mineral	Chemical Formula	Content, percent		Abundance in various magnetic complexes				
			Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Gran- ites	Alkali gran- ites and grano- syen- ites	Alkali neph- eline syen- ites	Alkalic ultra- basic rocks	Basic and ultra- basic rocks
I. Oxides									
BX <sub>2</sub>	Ilmenorutile	(Ti, Nb, Fe)O <sub>2</sub>	up to 32	up to 14.7	-	+	*	-	-
	Struverite	(Ti, Ta, Nb, Fe)O <sub>2</sub>	up to 9.3	up to 38.17	+	-	-	-	-
	Simpsonite	AlTaO <sub>4</sub>	0.33-6.05	60-72.31	+	-	-	-	-
	Belyankinite	(Ti, Zr, Nb, Mn, Fe)O <sub>2</sub> ·2H <sub>2</sub> O?	7-7.86		-	-	+	-	-
	Gerasimovskite	(Nb, Ti, Zr, Mn, Fe)O <sub>2</sub> ·2H <sub>2</sub> O?	43.91-44.90	0.38-0.50	-	-	x	-	-
ABX <sub>3</sub>	Dysanalite (Knopite, variety of perovskite)	(Ca, TR) (Ti, Nb)O <sub>3</sub>	4.7	0.02	-	-	+	*	-
	Loparite	(Na, Ce, Ca) <sub>2</sub> (Ti, Nb) <sub>2</sub> O <sub>6</sub>	7.09-9.75	0.51-0.65	-	-	*	-	-
	Nioboloparite	(Na, Ce, Ca) <sub>2</sub> (Ti, Nb) <sub>2</sub> (O, OH) <sub>6</sub>	26.6		-	-	x	-	-
	Irinite	(Na, Ce, Th) (Ti, Nb)O <sub>3</sub>	6.31		-	-	x	-	-
ABX <sub>4</sub>	Fergusonite	Y(Nb, Ta)O <sub>4</sub>	38.95-46.66	2-2.62	*	*	-	-	-
	Formanite	Y(Ta, Nb)O <sub>4</sub>	2.15	55.51	x	-	-	-	-
	Risorite	(Y, Er) (Ti, Nb, Ta)O <sub>4</sub>	-	-	x	+	-	-	-
	Bismutotantalite (Ugandite)	Bi(Ta, Nb)O <sub>4</sub>	6.46-14.76	31.14-41.15	x	-	-	-	-
	Stibiotantalite	Sb(Ta, Nb)O <sub>4</sub>	-	60.24	x	-	-	-	-
	Stibiocolumbite	Sb(Nb, Ta)O <sub>4</sub>	47.69	-	x	-	-	-	-
AB <sub>2</sub> X <sub>6</sub>	Columbite	(Fe, Mn)Nb <sub>2</sub> O <sub>6</sub>	>60	>20	*	+	x	-	-
	Mn-columbite	MnNb <sub>2</sub> O <sub>6</sub>	75.17	2.43	*	+	-	-	-
	Tantalocolumbite	(Fe, Mn) (Nb, Ta) <sub>2</sub> O <sub>6</sub>	40-60	40-20	*	-	-	-	-
	Niobotantalite	(Fe, Mn) (Ta, Nb) <sub>2</sub> O <sub>6</sub>	40-20	40-60	*	-	-	-	-
	Tantalite	(Fe, Mn)Ta <sub>2</sub> O <sub>6</sub>	<20	>60	*	-	-	-	-
	Mn-tantalite	(Mn, Fe)Ta <sub>2</sub> O <sub>6</sub>	5.04	71.10	*	-	-	-	-
	Ixiolite	(Mn, Sn) (Ta, Nb) <sub>2</sub> O <sub>6</sub>	-	-	*	-	-	-	-
	Alvarolite	MnTa <sub>2</sub> O <sub>6</sub>	-	-	x	-	-	-	-
	Mossite	Fe(Nb, Ta) <sub>2</sub> O <sub>6</sub>	0.2-0.3	84.9-85.3	*	-	-	-	-
	Manganomossite	Variety mossite, high Mn	82.55	-	x	-	-	-	-
	Tapiolite	Fe(Ta, Nb) <sub>2</sub> O <sub>6</sub>	1.37	82.55	x	-	-	-	-



## I. Oxides (continued)

		(Y, Ce, U, Ca) (Nb, Ti, Ta) <sub>2</sub> O <sub>6</sub> Variety euxenite, high in Ta Euxenite, in which Ta > Nb (Y, U, Th) (Nb, Ti, Fe) <sub>2</sub> O <sub>6</sub> (Ca, Ce, Na) (Nb, Ti, Fe, Al) <sub>2</sub> (O, OH, F) <sub>6</sub> (Y, Ce, U, Ca) (Ti, Nb, Ta) <sub>2</sub> O <sub>6</sub> Variety polycrase, high in Ta (Y, U) (Ti, Nb) <sub>2</sub> (O, OH) <sub>6</sub> Niobantalat of U and TR (Ce, Ca, Th) (Ti, Nb) <sub>2</sub> O <sub>6</sub> (Ce, La, Y, Th, Ca) (Ti, Zr, Nb, Ta) <sub>2</sub> O <sub>6</sub> (Y, Ce, Ca, Th) (Ti, Nb) <sub>2</sub> O <sub>6</sub> (Y, Ca, Th) (Nb, Ti) <sub>2</sub> O <sub>6</sub>	29.0 - 3.83 39.92 70.12-71.51 28.56 4.35 - - 23.8-32.5 11.90 - -	1.01 - 47.31 7.47 trace - 23.10 - - 0-6.9 1.35 - -	+	*	x	-	-
AB <sub>2</sub> X <sub>6</sub> (con- cluded)	Euxenite (Lyndochite) Eschweilite Tanteuxenite Khalopinite Fersmite Polycrase Tanpolycrase Kobeite Pisekite Eschynite Polymignite Blomstrandine Priorite								
A <sub>2</sub> B <sub>2</sub> X <sub>7</sub>	Pyrochlore (Chalcolamp- rite, endeiolite, pyrrhite) Koppite Marignacite Hatchettolite (Uran-pyro- chlore ellsworthite, samiresite) Microlite Tantal-hatchettolite Neontalite Stibiomicrolite Scheteligite	(Na, Ca) <sub>2</sub> (Nb, Ti) <sub>2</sub> O <sub>6</sub> (OH, F) Variety of pyrochlore, high in Ce <sub>2</sub> O <sub>3</sub> Hydrated variety of pyrochlore  (Na, Ce, Y, U) <sub>2</sub> (Nb, Ti, Ta) <sub>2</sub> (O, OH) <sub>7</sub> (Na, Ca) <sub>2</sub> (Ta, Nb, Ti) <sub>2</sub> O <sub>6</sub> (OH, F, O) Variety of microlite, high in U Variety of microlite, high Nb and Fe Variety of microlite, high Sb (Ca, Y, Sb, Mn) <sub>2</sub> (Ti, Ta, Nb) <sub>2</sub> (O, OH) <sub>7</sub>	56.16-62.52 - -  45.80 0.4-7.7 - 22 - 8.65	0.3-3.2 - -  3.70 67-77 - 57.7 - 20.0	x - -  x * x x * -	+	*	x	-
An (B <sub>2</sub> X <sub>7</sub> ) <sub>m</sub>	Betafite Mendeleevite Blomstrandine Dgalmaite Samaraskite (Yttrio- columbite, yttrio- niobite) Plumboniobite	(U, Ca, Ce, Y) (Nb, Ta, Ti) <sub>2</sub> (O, OH) <sub>7</sub> ? Variety betafite, with no Ti Variety betafite, high in Ta (U, Ca, Ce, Y) (Ta, Nb, Ti, Pb, Bi) <sub>2</sub> (O, OH) <sub>7</sub>  (Y, Er, U <sub>4</sub> ) [(Nb, Ta, Fe) <sub>2</sub> O <sub>7</sub> ] <sub>3</sub> (Y Yb, Gd) <sub>2</sub> (Fe, Pb, Ca, U) <sub>2</sub> (Nb <sub>2</sub> O <sub>7</sub> ) <sub>2</sub>	34.80 - 23.30 1.41  32.02 -	1.00 - 28.50 72.27  11.18 -	x x x x  +	-	-	-	-

<sup>1</sup> [TR= terres rares (French for rare earths)]



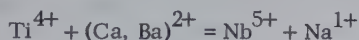
TABLE 5. Systematics of minerals of tantalum and niobium (concluded)

Type of For- mula	Mineral	Chemical Formula	Content, percent		Abundance in various magnetic complexes			
			Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	Gran- ites	Alkali- gran- ites and syenites	Alkali- neph- line sye- nites	Alkalic ultra- basic rocks
An (B <sub>2</sub> O <sub>7</sub> ) <sup>m</sup> (con- cluded)	I. Oxides (concluded)							
	Ishikawaite	Variety samarskite, high in U	36. 80	15. 00	x	x	-	-
	Ampangabeite (Vietinghofite)	Variety samarskite, high U, Fe, H <sub>2</sub> O	34. 80	8. 90	x	x	-	-
	Hielmite	Variety samarskite, high Ta, Sn, Fe, Mn, Cu	16. 35	54. 52	x	-	-	-
	Calcosamarskite	Variety samarskite, contains 7 percent CaO	-	-	x	x	-	-
	Loranskite	Variety samarskite, high Zr	-	-	x	x	-	-
	Hydrosamarskite	Variety samarskite, hydrated	-	-	x	x	-	-
Other Oxides	Yttrotantalite	Y <sub>4</sub> [Ta <sub>2</sub> O <sub>7</sub> ] <sub>3</sub>	-	-	x	-	-	-
	Thoreaulite	Sn[(Ta, Nb) <sub>2</sub> O <sub>7</sub> ]	-	72. 83	x	-	-	-
	Toddlite	(Y, U) (Ta, Nb, Fe) <sub>6</sub> O <sub>15</sub> · 2H <sub>2</sub> O	55. 73	8. 97	-	x	-	-
With (SiO <sub>4</sub> )	Metaloparite	(Ce, Ca) (Ti, Nb) <sub>2</sub> O <sub>5</sub> (OH)	10. 78	0. 66	x	-	+	-
	Wiikite	Ca <sub>3</sub> UNb <sub>3</sub> O <sub>12</sub> OH	38. 50	38. 50	x	x	-	-
	II. Silicates							
With (SiO <sub>4</sub> )	Fersmanite	(Ca, Na) <sub>2</sub> (Ti, Nb) [SiO <sub>4</sub> ](OH, F) <sub>3</sub>	15. 00	0. 36	-	-	+	-
	Wohlerite	(Ca, Na) <sub>3</sub> (Zr, Nb) <sub>2</sub> [SiO <sub>4</sub> ]F	5	1	-	x	-	-
	Epistolite	(Na, Ca) (Nb, Ti, Fe, Mn, Mg) [SiO <sub>4</sub> ](OH)	-	-	-	-	x	-
With (Si <sub>2</sub> O <sub>9</sub> )	Lomonosovite	Na <sub>2</sub> Ti <sub>2</sub> Si <sub>2</sub> O <sub>9</sub> . Na <sub>3</sub> PO <sub>4</sub>	3-6. 34	3-6. 34	-	-	*	-
	Murmanite	Na <sub>2</sub> Ti <sub>2</sub> Si <sub>2</sub> O <sub>9</sub> . nH <sub>2</sub> O	6. 56	0. 56	-	-	*	-
	Niocalite	Ca <sub>4</sub> NbSi <sub>2</sub> O <sub>9</sub> (O, F) <sub>2</sub>	16. 08	16. 08	-	-	x	-
With (Si <sub>2</sub> O <sub>7</sub> )	Nenadkevichite	(Na, Ca) (Nb, Ti) [Si <sub>2</sub> O <sub>7</sub> ] · 2H <sub>2</sub> O	24. 61	24. 61	-	-	+	-
	Shcherbakovite	(Na, K, Ba) <sub>3</sub> (Ti, Nb) <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ]	10. 44	10. 44	-	-	+	-
	Karnasurtite	(Ce, La) (Ti, Nb, Fe, Al) <sub>2</sub> [Si <sub>2</sub> O <sub>7</sub> ](OH) <sub>4</sub> · 3H <sub>2</sub> O	8. 20	8. 20	-	-	+	-

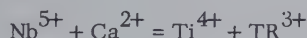
Notes: \* characteristic minerals  
+ abundant minerals  
x rarely-occurring minerals



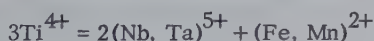
ionic radii (for  $Ti^{4+}$  - 0.64 Å). Rarely there occurs the isomorphous replacement of zirconium by niobium (wohlerite). The isomorphous replacement of titanium by niobium and tantalum has been established in minerals of the groups of loparite, rutile, euxenite-polycrase, aeschynite, priorite, samarskite, fergusonite, and also in titanio-niobo-silicates. In minerals of the perovskite group (loparite and others), nepheline, and titanio-niobo-silicates, compensation of charge for the isomorphous replacement of titanium by niobium is achieved mainly by the replacement of a corresponding number of ions of calcium or barium by sodium:



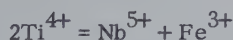
In pyrochlore, niobium is replaced by titanium, whereby there is simultaneous replacement of a corresponding amount of calcium by rare earths:



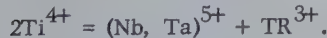
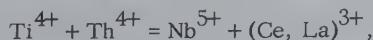
In the minerals of the rutile group (rutile, menenurite, strueverite, and others), during the isomorphous replacement of titanium by niobium and tantalum, valence compensation is attained by the entry into the crystal structure, along with niobium and tantalum, of a corresponding amount of iron or manganese:



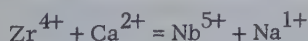
Part of the iron enters into minerals of the rutile group in the trivalent form, compensating the valence according to the scheme:



In minerals of the groups euxenite-polycrase, samarskite, and fergusonite, electrostatic compensation for the replacement of titanium by niobium and tantalum is obtained, apparently, by the replacement of a corresponding amount of thorium and uranium by rare earths:



In the replacement of zirconium by niobium in wohlerite, there proceeds simultaneously the replacement of calcium by sodium, as in loparite:



Besides the independent tantalio-niobium and complex tantalio-rare earth minerals, tantalum and niobium enter into other minerals in significant amounts (table 6).

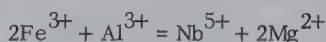
The highest contents of tantalum and niobium occur in minerals of titanium, zirconium, tin, tungsten, rare earths, and thorium. In the

form of significant admixtures, these elements together with titanium enter into minerals of iron and aluminum, and therefore, taking into account the wide distribution of the iron-magnesium pyroxenes, amphiboles, and micas, one may assume that most of the tantalum and niobium in nature is dispersed in precisely these minerals.

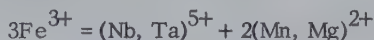
One of the principal features of the geochemistry of tantalum and niobium is their affinity with titanium. These elements not only form complex titanio-tantalio-niobium minerals, but also enter in the form of isomorphous admixtures into all titanium minerals. Hevesy (1929) established that the average atomic ratio of niobium to titanium in titanium minerals equals 1:3,000 and of tantalum to titanium 1:7,000.

In the replacement of titanium by tantalum and niobium in independent titanium minerals, compensation of valence is attained in different minerals in various ways. Thus, it is accomplished, both in rutile and in ilmenite by the simultaneous entry of divalent iron and manganese. In the entry of niobium into perovskite, electrical neutrality is attained, as also in loparite, by the simultaneous replacement of calcium by sodium with the formation of dysanaleite or by the replacement of a second atom of titanium by rare earths with the formation of knopite.

In the iron oxides (magnetite, titanomagnetite, hematite), and also chromite, vredenburghite, pyroxenes, amphiboles, chlorites, and micas, tantalum and niobium, together with titanium, apparently replace iron. Thereby in the silicates, electrical neutrality is probably attained by the simultaneous replacement of part of the silicon by aluminum or of aluminum by magnesium:



In the iron oxides, electrical neutrality is attained by the entry simultaneously with niobium of a corresponding amount of manganese or magnesium:



A second geochemical feature of tantalum and niobium is their relation to zirconium. According to Goldschmidt (1954), there is found a direct dependence between the contents of niobium and zirconium in igneous rocks, with the average contents of niobium equalling one-tenth of the contents of zirconium. This ratio was observed in granites, liparites, syenites, trachytes, and nepheline syenites. Goldschmidt states that such a constant ratio of niobium and zirconium is scarcely to be explained by the crystal structure of the minerals; probably niobium in the form of some stable complex anion with fluorine and oxygen is associated with cor-

# INTERNATIONAL GEOLOGY REVIEW

TABLE 6. Contents of Ta and Nb in various minerals

Name of Mineral	Formula	Maximum content percent		Author
		Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	
Oxides and Hydroxides				
Magnetite	Fe <sub>3</sub> O <sub>4</sub>	0.026	-	K. Rankama (1944)
Titanomagnetite	(Fe, Ti) <sub>3</sub> O <sub>4</sub>	0.055	0.002	K. Rankama (1944)
Chromite	FeCr <sub>2</sub> O <sub>4</sub>	-	0.00004	K. Rankama (1944)
Vredenburgite	(Mn, Fe) <sub>3</sub> O <sub>4</sub>	-	0.0001	K. Rankama (1944)
Ilmenite	FeTiO <sub>3</sub>	1.35	0.08	M. V. Kuxmenko
Hematite	Fe <sub>2</sub> O <sub>3</sub>	2.20	0.32	M. V. Kuzmenko
Perovskite	CaTiO <sub>3</sub>	4.7	0.02	K. Rankama (1944)
Rutile	TiO <sub>2</sub>	3.00	0.07	E. I. Semenov (1957) and K. Rankama (1944)
Anatase	TiO <sub>2</sub>	0.067	0.03	K. Rankama (1947)
Arkansite	TiO <sub>2</sub>	-	0.01	K. Rankama (1947)
Brookite	TiO <sub>2</sub>	3.44	3.44	E. I. Semenov (1957)
Cassiterite	SnO <sub>2</sub>	3.44	2.82	K. Rankama (1944) and Ya. D. Gotman (1941)
Pyrolusite	MnO <sub>2</sub>	-	0.0001	K. Rankama (1944)
Tungstates				
Wolframite	(Mn, Fe)WO <sub>4</sub>	5.	0.8	K. Rankama (1944)
Huebnerite	MnWO <sub>4</sub>	-	0.00006	K. Rankama (1944)
Phosphates				
Monazites	(Ce, La)PO <sub>4</sub>	-	0.004	K. Rankama (1944)
Triplite	(Mn, Fe) <sub>2</sub> PO <sub>4</sub> F	-	0.0009	K. Rankama (1944)
Amblygonite	LiAlPO <sub>4</sub> F	-	0.008	K. Rankama (1944)
Pyromorphite	Pb <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> Cl	-	0.00001	K. Rankama (1944)
Erikite	(Ce, La)(P, Si)O <sub>4</sub> ·H <sub>2</sub> O	0.90	-	Gerasimovsky (1937)
Silicates				
Topaz	AlSiO <sub>4</sub> (F, OH) <sub>2</sub>	-	0.001	K. Rankama (1944)
Zircon	ZrSiO <sub>4</sub>	2.	0.4	K. Rankama (1944)
Thorite	ThSiO <sub>4</sub>	0.31	0.02	K. Rankama (1944)
Sphene	CaTiSiO <sub>5</sub>	3.3	0.12	K. Rankama (1944, 1947)
Yttrotitanite	(Ca, Y, Ce)TiSiO <sub>5</sub>	1.2	0.0002	K. Rankama (1944)
Chevkinite	(Ca, Y, Ce)TiSiO <sub>5</sub>	-	0.0002	K. Rankama (1944)
Tourmaline	(Na, Ca)(Mg, Al) <sub>6</sub> Si <sub>6</sub> Al <sub>3</sub> B <sub>3</sub> (O, OH, F) <sub>30</sub>	0.007	0.0002	K. Rankama (1944)
Thortveitite	(Sc, Y) <sub>2</sub> Si <sub>2</sub> O <sub>7</sub>	0.95	2	K. Rankama (1944)
Astrophyllite	(K, Na) <sub>2</sub> (Fe, Mn) <sub>4</sub> (Ti, Zr)Si <sub>4</sub> O <sub>14</sub> (OH) <sub>2</sub>	2.15	0.008	K. Rankama (1944)
Lamprophyllite	Na <sub>2</sub> SrFeTi <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub> O	0.62	-	K. Rankama (1944)
Kupletskite	(K, Na) <sub>2</sub> Mn <sub>4</sub> (Si <sub>2</sub> O <sub>7</sub> ) <sub>2</sub> (OH) <sub>2</sub>	0.66	-	E. I. Semenov (1956)
Ramsayite	Na <sub>2</sub> Ti <sub>2</sub> Si <sub>2</sub> O <sub>9</sub>	0.50	0.09	Gerasimovsky (1936)
Eudialyte	(Na, Ca) <sub>6</sub> ZrSi <sub>6</sub> O <sub>17</sub> (O, OH, Cl)	2.35	0.1	K. Rankama (1944)
Eucolite	(Na, Ca) <sub>6</sub> ZrSi <sub>6</sub> O <sub>17</sub> (O, OH, Cl)	4.00	0.07	K. Rankama (1944)
Mangan	(Ce, La, Th)(Mn, Fe)SiO <sub>3</sub> (OH) <sub>2</sub> ·2H <sub>2</sub> O	2.00	-	M. V. Kuzmenko
Steenstrupine	(Ce, La, Th) <sub>2</sub> (Mn, Fe)(SiO <sub>3</sub> ) <sub>4</sub> ·5H <sub>2</sub> O	2.13	-	Gerasimovsky (1936)
Catapleute	Na <sub>2</sub> Zr(Si <sub>3</sub> O <sub>9</sub> )·2H <sub>2</sub> O	1.2	0.02	K. Rankama (1944)
Elpidite	Na <sub>2</sub> ZrSi <sub>6</sub> O <sub>12</sub> (OH) <sub>6</sub>	1.43	-	Tikhonenkov, et al. (1957)
Titanolavenite	(Na, Mn, Ca)(Zr, Ti)(SiO <sub>4</sub> ) <sub>2</sub> F	3.01	-	Kutukova (1940)
Riebeckite	Na <sub>2</sub> Fe <sub>3</sub> (FeSi <sub>4</sub> O <sub>11</sub> ) <sub>2</sub> (OH) <sub>2</sub>	0.0078	-	M. V. Kuzmenko
Diopside	CaMgSi <sub>2</sub> O <sub>6</sub>	-	0.00004	K. Rankama (1944)
Aegirine	NaFeSi <sub>2</sub> O <sub>6</sub>	0.013	0.0005	K. Rankama (1944)
Hypersthene	(Mg, Fe)Si <sub>2</sub> O <sub>6</sub>	-	0.0003	K. Rankama (1944)
Lamprobolite	Ca <sub>2</sub> Na(Mg, Fe, Ti)(Si, Al) <sub>4</sub> O <sub>11</sub> (OH) <sub>2</sub>	0.016	0.00005	K. Rankama (1944)
Muscovite	KAl <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>2</sub>	0.045	0.0011	M. V. Kuzmenko
Phlogopite	KMg <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (OH, F) <sub>2</sub>	-	0.00005	K. Rankama
Biotite	K(Mg, Fe) <sub>3</sub> AlSi <sub>3</sub> O <sub>10</sub> (F, OH) <sub>2</sub>	0.188	0.1	K. Rankama
Lepidolite	KLi <sub>2</sub> AlSi <sub>4</sub> O <sub>10</sub> (F, OH) <sub>2</sub>	-	0.007	K. Rankama
Polyolithionite	KLi <sub>2</sub> AlSi <sub>4</sub> O <sub>10</sub> (F, OH) <sub>2</sub>	0.40	-	M. V. Kuzmenko
Chlorite	(Mn, Fe) <sub>5</sub> Al(AlSi <sub>3</sub> )O <sub>10</sub> (OH) <sub>8</sub>	2.50	-	M. V. Kuzmenko
Nontronite	(Mg, Fe, Al)(Si <sub>4</sub> O <sub>10</sub> )(OH) <sub>2</sub> ·nH <sub>2</sub> O	0.01	-	Gerasimovsky (1936)

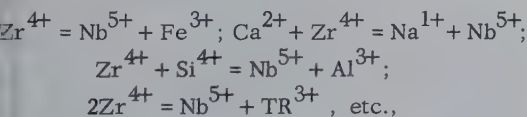


# M. V. KUZMENKO

TABLE 6. Contents of Ta and Nb in various minerals (concluded)

Name of Mineral	Formula	Maximum content percent		Author
		Nb <sub>2</sub> O <sub>5</sub>	Ta <sub>2</sub> O <sub>5</sub>	
Silicates (concluded)				
epherline	NaAlSiO <sub>4</sub>	-	0.00005	K. Rankama (1944)
arnet	Fe <sub>3</sub> Al <sub>2</sub> (SiO <sub>4</sub> ) <sub>3</sub>	0.025	-	M. V. Kuzmenko
ovchorrite	(Ca,Na) <sub>6</sub> (Ti,Ge) <sub>3</sub> (SiO <sub>4</sub> ) <sub>4</sub> (F,OH) <sub>4</sub>	2.6	-	T. A. Burova (1936)
ydrocerite	(Ce,La,Th) <sub>2</sub> (Si,P) <sub>2</sub> O <sub>7</sub> ·5H <sub>2</sub> O	2.56	-	M. V. Kuzmenko
abuntsovite	(K, Na, Ba)(Ti, Fe)Si <sub>2</sub> O <sub>7</sub> ·H <sub>2</sub> O	1.45	-	Semenov and Burova (1955)
irfesite	mZrO <sub>2</sub> ·nFe <sub>2</sub> O <sub>3</sub> ·pSiO <sub>2</sub> ·qH <sub>2</sub> O	2.40	-	Kostyleva (1945)
Other minerals				
raphite	C	-	0.0002	K. Rankama (1944)
phalerite	ZnS	-	0.00002	K. Rankama (1944)
luorite	CaF <sub>2</sub>	-	0.00003	K. Rankama (1944)
alcite	CaCO <sub>3</sub>	-	0.00002	K. Rankama (1944)
lunite	KAl <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	-	0.0001	K. Rankama (1944)

responding complex anions of zirconium. Tantalum and niobium in small amounts are present in zircon, alvite, cyrtolite, lavenite, hiortdahlite, eudialyte, eucolite, catapleite, and other zirconium minerals. In all these minerals, besides tantalum and niobium, there are nearly always present admixtures of other elements: Ti, Fe, Mn, Sr, TR, U, Sn, Be, K, OH, F. Consequently, compensation of valence in the replacement of zirconium by tantalum and niobium is accomplished either statistically at the expense of the entry into the mineral of other elements with lower valence:

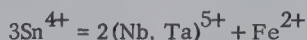


at the expense of the entry of fluorine, chlorine, and the hydroxyl group in the anionic part, which diminishes the charge on the compound, increased by the entry of the niobium.

Despite the presence of constant admixtures of tantalum and niobium in zirconium minerals and the constant ratios of these elements in igneous rocks, complex niobo-zirconium minerals (wohlerite) are very rarely formed in nature. In all probability, this is explained by the crystallochemical properties of tantalum, niobium, and zirconium. According to the rules of polar heterovalent isomorphism, it is energetically favorable to entrain tantalum and niobium in the crystal structure of its minerals, elements with higher valence and smaller sizes of ionic radius. However, the significant differences in sizes of ionic radius (for Zr 0.82 Å) limits the entry of tantalum and niobium into the crystal lattices of zirconium minerals, because unlimited isomorphism of these elements would cause the destruction of the crystal structure.

A third geochemical feature of tantalum and

niobium is their relationship to tin, which is explained by the closeness of the sizes of their ionic radii (Kuznetsov, 1947). Tantalum and niobium are always present in significant amounts in cassiterite, which is energetically favorable according to the rules of polar isomorphism; nevertheless, the differences in their chemical properties limits the range of isomorphism of these elements. For compensation of valence, divalent iron enters into the crystal lattice of cassiterite together with niobium and tantalum; its ionic radius is significantly larger (0.80 Å). This diminishes the energy of the crystal lattice of cassiterite and makes it less stable. The compensation of valence in this case is accomplished according to the scheme:



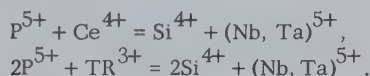
The entry of significant amounts of divalent iron, together with tantalum and niobium, into cassiterite probably leads to the decomposition of the compound with the formation of an isomorphous mixture of two isostructural minerals - cassiterite and tantalite-columbite. In nature such mixtures are known under the name "ainalite" and sometimes contain up to 10 percent (Ta,Nb)<sub>2</sub>O<sub>5</sub> and more. Despite the closeness of the sizes of the ionic radii of niobium, tantalum, and tin, complex tantaloniobotin minerals are practically not found in nature, except for the rarely occurring mineral thoreaulite, Ta<sub>2</sub>O<sub>5</sub>·SnO<sub>2</sub>, a double oxide of tantalum and tin, and hielmite, a stannotantalate of the rare earths, calcium, iron and manganese.

A fourth geochemical feature of tantalum and niobium is their relationship with tungsten, also explained by the closeness of the sizes of the ionic radii (for W<sup>4+</sup> 0.68 Å, for W<sup>6+</sup> 0.65 Å). Small admixtures of tungsten often are contained in minerals of tantalum and niobium; wolframite nearly always contains tantalum and niobium. In small amounts these elements are

present also in huebnerite and scheelite (Shcherbina, 1952). According to the rules of polar-directed heterovalent isomorphism, the endocryptic capture of hexavalent tungsten in the crystal lattices of minerals of niobium and tantalum as an element of higher valence is energetically favorable. However, in nature, the reverse phenomenon is more abundant -- the entry of tantalum and niobium into the crystal lattices of tungsten minerals, which does not correspond to these rules. In all probability, in the given case there takes place isomorphism between complex anions of tungsten and niobium.

It is possible that the observed high concentrations (5-10 percent) of niobium in wolframites are explained by the formation of mixed crystals of columbite and wolframite, which absolutely deserves study.

Besides minerals of titanium, zirconium, tin, and tungsten, tantalum and niobium are present in significant amounts in minerals of the rare earths and thorium. The presence of tantalum and niobium in monazite and rhabdophane is probably explained by the entry of these elements for the compensation of valence during the replacement of phosphorus by silicon, the ionic radii of which are close:



In minerals of the groups of steenstrupine, hydrocerite, and thorite, the presence of niobium is apparently explained by its entry to compensate valence during the replacement of quadrivalent thorium ( $r=0.95 \text{ \AA}$ ) by trivalent cerium ( $r=1.02 \text{ \AA}$ ) or lanthanum ( $r=1.04 \text{ \AA}$ ) according to the scheme:



K. Rankama (1944) explains the presence of tantalum in thortveitite,  $(\text{Sc}, \text{Y})_2\text{Si}_2\text{O}_7$ , by the isomorphous replacement of trivalent scandium ( $r=0.85 \text{ \AA}$ ) by pentavalent tantalum. The small admixtures of tantalum and niobium in other minerals (graphite, fluorite, calcite, alunite, topaz, etc.) are probably explained by contamination of the analyzed material.

#### BEHAVIOR OF TANTALUM AND NIOBIUM IN VARIOUS MINERAL-FORMING PROCESSES

Tantalum and niobium, in consequence of the similarity of their geochemical properties, are continually associated in nature, although their quantitative ratio in different mineral-forming processes varies to a significant degree. As mentioned by Goldschmidt (1954), in the process of differentiation of parental magmas, the contents of tantalum and niobium increase

from the ultrabasic and basic rocks to the acid and alkalic rocks. Only in acid and alkalic magmas does the concentration of tantalum and niobium become sufficient for the formation of independent minerals and deposits.

Both in the acid and in the alkalic complexes, rocks of increased concentration of tantalum and niobium are formed in magmatic, pegmatitic, pneumatolytic-hydrothermal, contact-metasomatic, and exogene processes (table 7); nevertheless, in each of these complexes, the behavior of tantalum and niobium in one and the same processes is different.

#### Magmatic Processes

In acid (granitic) complex rocks, the contents of the sum of tantalum and niobium increase at the end of the magmatic and further with the pegmatitic processes. In other words, in the process of formation of complex multiphase granitic intrusives the highest concentrations of tantalum and niobium are observed in the final phases of the intrusion and crystallization of the magma.

According to the data of K. Rankama (1947), the average content of niobium in granites equals 21 ppm, which is somewhat lower than its clark value for igneous rocks (24 ppm), and the average content of tantalum is 4 ppm, twice its clark value (2.1 ppm). In granitic massifs, tantalum and niobium are mostly dispersed in the iron-bearing titanium-containing minerals, and also the titanium- and zirconium-minerals; biotite, hornblende, magnetite, hematite, ilmenite, rutile, and zircon; and only an insignificant part of them under specific conditions form independent minerals, predominantly of the tantalite-columbite group, rarely samarskite and euxenite polycrase.

Studies by E. B. Znamensky (1957) and the author showed that the ratio of niobium to tantalum in accessory titanium and iron-titanium-bearing minerals of granites varies from 5 to 15 (table 8).

In zircons and rarely in ilmenites from provinces characterized by increased concentrations of tantalum, the contents of the latter sometimes predominate over those of niobium. The ratio of tantalum to niobium in granites increases from the early to the later phases of intrusion (Znamensky, 1957). Thus, in the process of magmatic evolution of granitic intrusives there is noted a tendency towards the enrichment of tantalum in the final products of crystallization.

In the last phases of formation of granitic massifs during the formation of small intrusives, there are usually expressed weakly the pegmatitic processes, but intensively the phenomenon of albitization, the concentrations



# M. V. KUZMENKO

TABLE 7. Scheme of genetic classification of deposits and ore manifestations of tantalum and niobium

Process	Granites	Alkali granites and granosyenites	Nepheline and alkali syenites	Alkalic ultra-basic rocks
Pegmatitic	Biotite granites w/ columbite (Joss Plateau, N. Nigeria). Granites with euxenite and polycrase (Altay)	Alkali granites w/ pyrochlore (Kaho, N. Nigeria). Alkali granites with fergusonite (Kiev, Kola Peninsula)	Urtites, lujavrites, and yuvites with loparite (Lovozero, Kola Peninsula). Miaskites with pyrochlore (Central Ural)	Pyroxenites and olivinites w/ perovskite (Kola Peninsula; Magnet Cove, Arkansas).
Pegmatitic	Undifferentiated and unreplaced pegmatites with columbite Little differentiated replaced pegmatites with tantalocolumbite (Transbaikal) Unreplaced differentiated pegmatites w/ niobotantalites (Paraiba, Brazil). Differentiated complex replacement pegmatites, w/ tantalite, microlite, simpsonite, cassiterite, (Sintsyan, Kalba, Kola Peninsula, S. Rhodesia)	Pegmatites with fergusonite (Kiev, Kola Peninsula; northern Vostok, U. S. S. R. )	Nepheline-feldspar and feldspar pegmatites with pyrochlore (Middle Urals) Feldspar pegmatites with pyrochlore, fersmite, and ilmenorutile Feldspar-aegirine pegmatites w/ lovorrite (Khibina, Kola Peninsula)	Rutile-brookite pegmatites (Magnet Cove, Arkansas)
Hydrothermal vein	Feldspar-quartz veins w/ cassiterite, scheelite, columbite (Kalba, South Dakota) Greisens with cassiterite, wolframite, molybdenite, columbite. (Kazakhstan, Far East)	Feldspar-quartz hematite veins w/ ilmenorutile and columbite (Middle Timan)	Albites with pyrochlore (Ukraine, Urals) Biotite and calcite veins with pyrochlore (Middle Urals)	Feldspar-calcite veins with rutile and brookite (Magnet Cove, Arkansas) Carbonatites with knopite (Magnet Cove, Arkansas) Carbonatites with pyrochlore and hatchettolite (Sukulu, Africa; Karelia)
Hydrothermal metasomatic	Albitized zones in granites with columbite-tantalite (Kalba) Greisenized zones in granites with columbite-tantalite, samarskite, euxenite, etc. (Ezopa Range and Tuloma R., Far East)	Albitized zones in granosyenites w/ polycrase (Tuva)	Albitized zones in alkalic rocks with pyrochlore (Ukraine) Carbonatized zones with pyrochlore (Middle Urals)	Natrolitized and biotitized zones in ijolites with knopite (Oka, Quebec) Carbonatized zones with pyrochlore (Mbeya, Africa)
Contact-metasomatic			Albitized nephelinized zones with perovskite, pyrochlore, at contacts of alkalic rocks with carbonates (Oka, Quebec; Kaiserstuhl, Germany)	
Diagenetic	Cassiterite, columbite-tantalite placers (Nigeria, Kalba) Samarskite placers (Altay) Ilmenitic placers (Ukraine)		Zircon - pyrochlore placers (Sukulu, Bukusu, Uganda) Ilmenite - rutile placers (Urals) Bauxites with ilmenite (Arkansas)	

# INTERNATIONAL GEOLOGY REVIEW

Table 8. Ratio of Nb to Ta in accessory minerals of granite

Mineral	Content, percent		Nb/Ta	Author
	Nb	Ta		
Ilmenite (Kalba)	0.086-0.36	0.013-0.064	5.6-6.6	E. B. Znamensky
Ilmenite (Cent. Kazakhstan)	0.945	0.064	14.8	M. V. Kuzmenko
Biotite (Kalba)	0.008-0.02	0.00076-0.026	7.2-12	E. B. Znamensky
Hematite	1.54	0.26	5.9	M. V. Kuzmenko
Zircon	0.007	0.011	0.6	E. B. Znamensky

of tantalum and niobium increase ten to one hundred fold as compared to the clarkes for igneous rocks (up to 0.2 percent (Ta, Nb<sub>2</sub>O<sub>5</sub>)) and they form independent minerals of the tantalite-columbite group in amounts sometimes having commercial significance (Northern Nigeria).

In the minerals of the tantalite-columbite group from albitized granites there is usually found a sharp preponderance of niobium over tantalum. The content in them of Ta<sub>2</sub>O<sub>5</sub> is 3 percent (2.45 percent Ta) with a ratio of Ta to Nb of approximately 1 to 25. This low ratio of Ta to Nb in the columbites when the granite itself has a ratio of 1 to 10 is probably explained by the predominant capture of tantalum by zircon or other accessory minerals. In particular, the ratio of Nb to Ta in hematite from such granites is sometimes 6. This problem deserves more careful study.

In greisenized granites, tantalum and niobium, besides columbite, sometimes form titanoniobates of the rare earths, uranium, and thorium, of the samarskite and euxenite-polycrase groups.

The problem of the content of Ta and Nb in alkalic granites, granosyenites, and syenites has not been studied up to now. According to the data of K. Rankama (1947), the average content of Nb in syenites is 35 ppm and of Ta 2 ppm, with a ratio Nb/Ta=17.5.

These rocks are usually characterized by increased contents of rare earths, uranium, and thorium, so that the tantalum and niobium in them, besides entering into the titanium-containing and zirconium minerals, form complex minerals -- titano-tantaloniobates of the rare earths, uranium, and thorium (samarskite, fergusonite, euxenite, polycrase, etc.), rarely pyrochlore. In exceptional cases, tantalum and niobium are concentrated in alkalic granites predominantly as pyrochlore (the riebeckite granites of Northern Nigeria), for the formation of which a medium enriched in calcium is necessary. The geological conditions of formation of the massif of riebeckite granite of Northern Nigeria is not yet clear; one may assume that in the process of their formation there took place an enrichment of the granitic magma in calcium at the expense of the assimilation of enclosing rocks rich in calcium.

In nepheline syenites, according to the data of K. Rankama (1947), the average content of niobium is 310 ppm, and of tantalum 0.8 ppm. As already noted, the contents of tantalum and niobium in various alkalic massifs vary in wide limits, and the numbers given by K. Rankama for these elements on the basis of two chemical analyses are scarcely to be called convincing. Especially so is the magnitude of the average content of tantalum.

In alkalic and nepheline syenites, tantalum and niobium, besides entering into aegirine, arfvedsonite, biotite, and lepidomelane, are concentrated in the minerals of titanium (ilmenite, sphene, ramsayite, lamprophyllite, etc.) and of zirconium (eudialyte, eucolite, lovozerite, zirkelite, zircon), and form independent niobium minerals (pyrochlore) and also complex minerals with titanium and rare earths (loparite, murmanite, lomonsovite, etc.). The most abundant minerals of niobium are loparite and pyrochlore. Independent tantalum minerals are not found in nepheline syenites. Loparite is characteristic of highly differentiated massifs of nepheline syenites that contain calcium in amounts below its clark (Lovozero). In nepheline syenites that are enriched in calcium, tantalum and niobium, besides being dispersed in dark titanium-containing minerals, are concentrated in the titanium and zirconium -- sphene and eudialyte (Khibina -- Burova, 1936; Borodin, 1955; Pantel'ev, 1938) or form independent niobium minerals -- pyrochlore (Urals).

As already established by V. I. Gerasimovskiy (1957) for the example of the Lovozero alkali massif, the ratio of niobium to tantalum in niobium and niobium-containing minerals of nepheline syenites and also in the nepheline syenites themselves varies from 9 to 15.4, i.e., corresponds to the ratios given by K. Rankama and T. Sahama (1949) for the main types of magmatic rocks (5 for granites and up to 17.3 for gabbro). Thus, the assumption of Goldschmidt (1954) and K. Rankama on the separation of tantalum and niobium and the predominant concentration of the latter in alkalic magmas must be stated to be erroneous. If one takes the average content of niobium in nepheline syenites after Rankama to be 310 ppm and for the average ratio of Nb to Ta 11-12, we obtain for the average content of tantalum 26 ppm, which is 6 times as high as its average content in granites and 12.4 times the clark of tantalum for igneous rocks; the concentration of niobium is also ap-



approximately 13 times higher than its clark.

The numbers given are approximate and require further refinement; nevertheless it is evident that in alkalic magmas there occurs the concentration not only of niobium, but also of tantalum.

In alkalic ultrabasic rocks the average content of Nb, according to the data of Rankama (1947), is 14 ppm and of Ta 1.2 ppm, with a ratio Ta to Nb = 1:8.3. Thus, in these rocks the concentrations of Nb and Ta are nearly equal to their clarkes for igneous rocks. Tantalum and niobium do not form independent minerals in alkalic ultrabasic rocks, but are concentrated in titanium-containing iron-, titanium-, and to a lesser degree zirconium-minerals -- titanomagnetite, perovskite, ilmenite, pyroxenes, etc.

The behavior of Ta and Nb in ultrabasic rocks has not been studied. According to the data of Rankama (1947) the Nb<sub>2</sub>O<sub>5</sub> content in them is 23 ppm (or 16 ppm Nb) and of Ta 1 ppm, with a ratio Nb:Ta = 16:1. Tantalum and niobium do not form independent minerals in the ultrabasic rocks, but are dispersed in the minerals of titanium and perhaps of iron (ilmenite, pyroxenes, magnetite, etc.).

#### Pegmatitic Processes

In pegmatites of granitic complexes there are found concentrations of tantalum with respect to niobium. Granitic pegmatites are at present the only source of tantalum ores. The contents of combined tantalum and niobium in them increases at the end of the pegmatitic processes, mainly because of increase in the concentration of tantalum, and the ratio of tantalum to niobium increases in the same direction. Tantalum and niobium are dispersed to a small degree in micas, garnets, and tourmalines, also in ilmenites and zircons, but mostly they form independent minerals, predominantly of the columbite-tantalite group.

The ratio of tantalum to niobium in granitic pegmatites depends on the ratio of these elements in the original pegmatitic melt. Pegmatitic fields occur in which tantalum predominates, others in which niobium predominates. In the majority of cases, the ratio Ta/Nb in granitic pegmatites varies from 1:2 to 2:1, and the concentration of tantalum in them may reach 0.02-0.03 percent, which is approximately 10 times its clark.

The behavior of tantalum and niobium in granitic pegmatitic processes is determined mainly by the concentrations and ratios of these elements in the original melt, the degree of differentiation of the pegmatite body, and the intensity of the phenomenon of replacement. Nevertheless, for most pegmatitic fields there

are marked specific regularities of the distribution of tantalum and niobium.

In high-temperature equigranular undifferentiated and unreplaced pegmatites, the tantaloniobates usually occur in small amounts in the form of columbite. In lower-temperature blocky and semi-differentiated pegmatites, the amount of tantaloniobate and the ratio in it of Ta/Nb are increased and they consist mainly of tantalumbearing columbite and niobium-bearing tantalite (Ginzburg, 1956). In tantalum provinces in such pegmatites tantalite sometimes appears in large amounts at the contact of the mono-mineralic microcline [microcline] zone with the quartz core.

In intensively replaced pegmatites the contents of tantalum and niobium are higher, but their ratio varies according to the specific case. In weakly differentiated, intensively replaced pegmatites, niobium usually predominates over tantalum or their ratio is close to 1:1. In semi-differentiated, intensively replaced pegmatites, tantalum predominates over niobium, and the minerals of these elements are predominantly niobotantalite and tantalite. In the replacement complex, in the case of the development of lepidolite aggregates, there are present microcline, ampanagabeite, stibiotantalite, simpsonite, bismutotantalite, thoreaulite, and others, and tantalite is present as its manganese variety, manganotantalite. The ratio Ta/Nb in the tantaloniobates of different replacement complexes may vary, but in most cases it is highest in the lepidolite complexes, somewhat lower in the muscovite and quartz-muscovite, and even lower in the albitic. In the last two complexes, the reverse relation is sometimes found.

In the last stages of the pegmatitic processes -- the replacement stage -- tantalum and niobium not only form independent minerals, but enter isomorphously into cassiterite, scheelite, and wolframite (in amounts of whole percents), in which they replace isomorphously tin and tungsten. In wolframite niobium always sharply predominates over tantalum, but at the same time there is often observed the reverse relation. The concentrations of tantalum in the replacement complex of granitic pegmatites sometimes reaches 0.4 percent, which is about 1,900 times the clark of tantalum for igneous rocks. In intensively replaced pegmatites on the whole, the concentrations of Ta and Nb usually are 10 to 100 times their clarkes.

It must be noted that in the granitic pegmatites, as in the greisens, there is observed a close paragenesis of tantalum with lithium. Predominance of tantalum over niobium is generally characteristic for lithium-bearing pegmatitic fields, and in single pegmatitic bodies, for lepidolitic replacement complexes. The geochemical nature of such a relationship is not known at present.

In the pegmatites of alkalic granites and granosyenites, tantalum and niobium occur in close association with titanium, rare earths of the yttrium subgroup, and uranium; they form complex minerals: titano-tantalo-niobates of the rare earths of the groups of euxenite, polycrase, fergusonite, samarskite, etc. The concentrations of tantalum, niobium, and other rare elements in granosyenitic pegmatitic processes, as in the granitic, increases towards the end -- towards the stage of replacement with which are associated most of the tantalo-niobates of rare earths and other rare-metal minerals.

In alkalic pegmatites tantalum and niobium are associated with titanium, rare earths, and thorium, with which they sometimes form complex minerals -- loparite, aeschynite, fersmite, ilmenorutile, lomonosovite, murmanite, lovchorrite, rinkolite, karnasurtite, etc. Independent niobium minerals in alkalic pegmatites are pyrochlore, nioboloparite, epistolite, and nenadkevichite. Besides, tantalum and niobium enter in small amounts the crystal structures of minerals of titanium and zirconium -- sphene, ilmenite, rutile, ramsayite, lamprophyllite, enigmatite, zircon, eudialyte, etc. The ratio of tantalum to niobium in the niobium minerals of pegmatites has not been sufficiently studied; individual determinations show that it varies from 1:10 to 1:20.

In the early stages of crystallization of alkalic pegmatites, tantalum and niobium do not usually form independent minerals and along with titanium enter as isomorphous admixtures into pyroxenes and amphiboles. In the pneumatolytic stage these elements form complex titano-niobium minerals, predominantly silicates, or enter isomorphously into minerals of titanium and zirconium. In a later stage -- the replacement stage -- tantalum and niobium form independent niobium minerals or complex minerals with the rare earths. The amount of the tantalo-niobium minerals increases towards the end of the pegmatitic process and reaches its maximum in the replacement stage.

In such alkalic massifs, where most of the tantalum and niobium precipitated in the magmatic stage (Lovozero), an increase of the concentrations of these elements is not observed at the end of the pegmatitic process, and most of them precipitate in the pneumatolytic stage of formation of alkalic pegmatites, in the form of murmanite, nenadkevichite, and epistolite.

In the alkaline ultrabasic complex rocks, the pegmatitic processes have not been studied. If one takes as analogous to pegmatites in these massifs the apatite-olivine-titanomagnetite bodies that often cut the ultrabasic rocks, then one must note that in these bodies tantalum and niobium do not form independent minerals, but are concentrated in the titaniferous iron and the titanium minerals (knopite, titanomagnetite,

pyroxenes, etc.), in which they isomorphously replace titanium. The ratio of tantalum to niobium in these minerals has not been studied; the data of Rankama (1944, 1947) indicate that the ratio of  $Ta_2O_5$  to  $Nb_2O_5$  in titanomagnetites is approximately 1:27. The presence of pyrochlore, sometimes observed in titanomagnetite bodies, is probably associated with later processes of carbonatization and mica formation.

#### Pneumatolytic-Hydrothermal Processes

In acid pneumatolytic-hydrothermal processes the highest concentrations of tantalum and niobium are observed in the high-temperature formations, and they decrease at the end of the process as the temperatures of the solutions decrease. The behavior of tantalum and niobium in pneumatolytic-hydrothermal processes depends on their concentrations in the incoming solutions, and also on the contents in these solutions of tungsten and tin.

In deposits formed as the result of sodium and potassium metasomatism (albitization and greisenization) of granites and aplites, tantalum and niobium usually form independent minerals of the groups of tantalite - columbite or samarskite and euxenite. The ratio of tantalum to niobium in the minerals is usually high and corresponds to the ratios of these elements in the tantalo-niobates formed in granitic pegmatites in the stage of albitization.

In quartz vein-greisen formations, enriched in tin and tungsten, tantalum and niobium are concentrated in wolframite, scheelite, and cassiterite, and in these cases, when the amounts of tantalum and niobium in solution exceed the limit of isomorphous miscibility with tin and tungsten, there are formed tantalo-niobates of the tantalite-columbite group. This mineral is often found in close intergrowth with cassiterite and wolframite.

In distinction from the pegmatites, in cassiterite and wolframite of pneumatolytic-hydrothermal deposits the contents of  $(Ta, Nb)_2O_5$  are tenths of a percent and niobium always predominates over tantalum. The ratio of  $Ta_2O_5$  to  $Nb_2O_5$  in cassiterites, judging from individual determinations, varies from 1:2 to 1:11, and nearly always equals 1:10 (as in wolframites). An exception to this ratio are the lepidolitic greisens, in the cassiterites of which the ratio of tantalum to niobium is unity or higher.

In the lower-temperature sulfide-cassiterite veins, the content of combined pentoxides of tantalum and niobium in the cassiterites is hundredths of a percent. In the sulfides, according to the data of Rankama (1944, 1947), tantalum is entirely absent, but niobium is sometimes noted in amounts of ten-thousandths and millionths of a percent. K. Rankama (1947) supposes that niobium in sulfides was absorbed



in solution in the form of the highly soluble canioabates  $\text{NaNbO}_3$  and  $\text{KNbO}_3$ .

In alkalic-acid (granosyenitic) pneumatolytic-hydrothermal processes, tantalum and niobium are closely associated with rare earths, uranium, zirconium. In albitites and metasomatic formations associated with processes of albitization, tantalum and niobium form complex rare earth-tantalo-niobium minerals of the ferrocolumbite or euxenite groups, with low contents of Ta. The ratio of  $\text{Ta}_2\text{O}_5$  to  $\text{Nb}_2\text{O}_5$  in these minerals is approximately 1:30. In hematite-quartz veins, tantalum is nearly entirely absent, but niobium forms columbite, closely associated with ilmenorutile, magnetite, hematite, and minerals of uranium, thorium, and rare earths.

In alkalic pneumatolytic-hydrothermal processes, the behavior of tantalum and niobium depends on the behavior of these elements in high-temperature processes -- magmatic and pegmatitic. In massifs where most of the tantalum and niobium are associated in the form of lopate in the magmatic stage (Lovozero) the concentrations of these elements decreases in the later stages -- pegmatitic and pneumatolytic-hydrothermal. In the pneumatolytic-hydrothermal processes, tantalum and niobium are fixed in small amounts in the form of complex rare earth-titanium-niobium silicates and apatophosphates.

In alkalic massifs, where the concentrations of tantalum and niobium are insufficient to precipitate most of them, there is observed an increase of the concentration of these elements in the pegmatitic and pneumatolytic-hydrothermal processes (Middle Urals). In albitites, ilmenite veins, and metasomatic albitized zones of such massifs, showing higher-temperature pneumatolytic-hydrothermal formations, the concentrations of tantalum and niobium are approximately the same as in the albitization stage of the pegmatitic processes, which confirms the genetic association of the pneumatolytic-hydrothermal sodium solutions with pegmatitic processes.

In the lower-temperature calcite-, biotite-, and composite carbonate-mica formations, the contents of tantalum and niobium are variable. In some cases they may be very high and exceed the contents of these elements in pegmatites; in other cases they are practically absent or are present in small amounts. High concentrations of tantalum and niobium in carbonate formations probably explain the secondary enrichment of the latter in processes of predominantly uranium metasomatism. Tantalum and niobium in pneumatolytic-hydrothermal processes in such cases are fixed in the form of the mineral pyrochlore and enter isomorphously into the niobium minerals (sphene, ilmenite, rutile), together with titanium into biotite.

In the pneumatolytic-hydrothermal stage of alkalic ultrabasic processes, expressed in sodium- and carbonate-metasomatism and the formation of vein bodies of carbonatites (Sukulu, Africa; Buori-Yarvi, Kola Peninsula), the concentrations of tantalum and niobium increase towards the end of the process, which is probably explained by secondary enrichment of the pneumatolytic-hydrothermal solutions in these elements. In the higher-temperature sodium solutions, the concentrations of tantalum and niobium, in all probability, were insufficient for the formation of independent minerals, but in the process of sodium metasomatism the composition of these solutions changed. They were set free from the sodium and enriched in calcium, magnesium, and iron, and also in tantalum and niobium, extracting the latter from the high temperature titanium and titanium-containing minerals (titanomagnetite, perovskite, pyroxene, etc.). Tantalum and niobium in the carbonatites are fixed in the form of minerals of the pyrochlore group or form complex minerals with zirconium.

#### Exogene Processes

Minerals of tantalum and niobium, and also minerals of titanium, zirconium, tin, and tungsten containing tantalum and niobium are stable and thereby in the process of the weathering of rocks are accumulated in deluvial-eluvial, alluvial, fluvio-glacial and marine placers, and also in bauxites of the crust of weathering of alkalic massifs, and kaolins. The concentrations of tantalum and niobium in placers and bauxites are ten times their clarkes. The principal minerals that concentrate these elements in placers are tantalo-niobates of the tantalite-columbite group, minerals of the euxenite group, pyrochlore, rutile, ilmenite, cassiterite, and wolframite.

#### CONCLUSIONS

1. Tantalum and niobium in consequence of the closeness of chemical and crystallochemical properties in all natural processes accompany one another.
2. Both elements are typically oxyphile and in processes of mineral formation reveal geochemical relationships to iron, manganese, titanium, rare earths, uranium, thorium, zirconium, tungsten, tin, bismuth, and antimony, with which they form complex minerals or enter isomorphously into their minerals. Tantalum shows closer relations to zirconium, tin, uranium, and rare earths of the yttrium subgroup, whereas niobium is more closely associated with titanium, tungsten, thorium, and rare earths of the cerium group.
3. Tantalum and niobium in natural processes accompany the alkali metals, especially Na and Li, with tantalum more closely asso-

ciated with lithium, and niobium with sodium.

4. The closeness of the crystallochemical and chemical properties of tantalum, niobium, and titanium explains the unlimited isomorphism of these elements in mineral-forming processes and the constant presence of tantalum and niobium in titanium minerals.

5. Zirconium, tungsten, and tin entrain tantalum and niobium in the crystal lattices of their minerals in limited amounts, which is explained by the significant differences of their chemical properties or the sizes of the ionic radii.

6. In the course of the evolution of a magma, the concentrations of tantalum and niobium increase from the ultrabasic to the acid rocks and further to the alkalic.

7. In all of the main types of rocks including granites, niobium greatly predominates over tantalum, and the ratio of niobium to tantalum ranges from 5 in some granitic massifs to 17 in basic and ultrabasic rocks; nepheline syenites have an intermediate position.

8. In all natural processes, excepting granitic pegmatites, niobium greatly predominates over tantalum. Only in granitic pegmatites, especially in the lithium-bearing ores, tantalum is the dominant element.

9. In acid (granitic) rock complexes, tantalum and niobium are closely associated with iron, manganese, and to a lesser degree with bismuth, antimony, tungsten, and tin; they form with these elements complex minerals or enter into their minerals.

10. In granosyenitic complexes, tantalum and niobium form complex minerals with titanium, rare earths of the yttrium subgroup, uranium and to a lesser degree with thorium.

11. The concentrations of tantalum and niobium in granitic and granosyenitic complexes increase towards the end of the magmatic and pegmatitic processes, and afterwards diminish towards the end of the pneumatolytic-hydrothermal processes.

12. In alkalic complexes, tantalum and niobium are closely associated with titanium, rare earths of the cerium group, and thorium, with which it forms complex minerals, and enters into titanium and zirconium minerals.

13. The concentrations of tantalum and niobium in alkalic massifs depend on magmatic crystallization differentiation. In highly differentiated massifs with high contents of tantalum and niobium, most of these elements precipitate during the magmatic process and afterwards in the pegmatitic and pneumatolytic-

hydrothermal; their concentrations gradually decrease. In weakly differentiated alkalic massifs less enriched in tantalum and niobium, the concentrations of these elements increase towards the end of the pegmatitic process and remains high to the end of the pneumatolytic-hydrothermal processes.

14. In alkalic ultrabasic complexes, in magmatic and pegmatitic processes, tantalum and niobium do not form independent minerals, but enter in small amounts into minerals of titanium and iron -- perovskite, titanomagnetite, and pyroxenes. At the end of the pneumatolytic-hydrothermal processes, the concentrations of tantalum and niobium in the solutions are increased, probably at the expense of the secondary enrichment of the pneumatolytic-hydrothermal solutions on the process of sodium metasomatism, as the result of which there are formed minerals of the pyrochlore group.

15. In ultrabasic complexes, tantalum and niobium do not form independent minerals, but are associated with minerals of titanium and iron in the magmatic process.

## REFERENCES

- Boky, G. B., 1956, [PRINCIPLES OF CLASSIFICATION OF CHEMICAL COMPOUNDS, INCLUDING MINERALS]: *Geokhimiya*, no. 6.
- Borodin, L. S., 1955a, [MINERAL INDICATORS OF NIOBIUM IN NEPHELINE SYENITES]: *Doklady Akad. Nauk SSSR*, 103, no. 5.
- \_\_\_\_\_, 1955b, [SOME FEATURES OF THE CONCENTRATION OF NIOBIUM IN NEPHELINE SYENITES]: *Doklady Akad. Nauk SSSR* 103, no. 6.
- Burova, T. A., 1936, [NIOBIUM IN THE Khibina AND LOVOZERO MINERALS (TITANO- AND ZIRCONO-SILICATES)]: *Geochemistry of Khibina tundra*, v. 2, Moscow-Leningrad, Izd. Akad. Nauk SSSR.
- Gerasimovsky, V. I., 1936, [THE MINERALOGY OF THE SOUTHEASTERN PART OF THE LUJAVRITES]: *Trudy Lomonosov Inst. Akad. Nauk SSSR*, no. 7.
- \_\_\_\_\_, 1937, [ERIKITE FROM THE LOVOZERO TUNDRA]: *Tr. Lomonosov Inst. Akad. Nauk SSSR*, no. 10.
- \_\_\_\_\_, 1956, [GEOCHEMISTRY AND MINERALOGY OF NEPHELINE-SYENITE INTRUSIVES]: *Geokhimiya*, no. 5.
- Gerasimovsky, V. I., Kakhana, M. M., and Rodionova, L. M., 1957, [THE RATIO OF NIOBIUM AND TANTALUM IN AGPAITIC ROCKS OF THE LOVOZERO ALKALIC MASSIF]: *Geokhimiya*, no. 7.



- enzburg, A. I., 1956, [SOME FEATURES OF THE GEOCHEMISTRY OF TANTALUM AND TYPES OF TANTALUM MINERALIZATION]: *Geokhimiya*, no. 3.
- oldschmidt, V. M., 1933, [PROBLEMS AND METHODS OF GEOCHEMISTRY] in: [MAIN IDEAS OF GEOCHEMISTRY]: v. 1, Goskhimtekhn-izdat.
- \_\_\_\_\_, 1954, *Geochemistry*: Oxford.
- otman, Ya. D., 1941, [TYPOMORPHIC FEATURES OF CASSITERITE TIN -- MINERALIZED DEPOSITS OF U.S.S.R.]: *Trudy Inst. geol. nauk. Akad. Nauk SSSR*, no. 46, Ser. min., no. 9.
- evsey, G. V., Alexander, E., and Wurstlin, K., 1929, *Z. anorg. allg. Chem.* 181, 95.
- ostyleva, E. E., 1945, [ZIRFESITE, A NEW ZIRCONIUM MINERAL OF THE SUPER-GENE ZONE]: *Doklady Akad. Nauk SSSR*, 48, no. 7.
- utukova, E. I., 1940, [TITANO-LAVENITE OF THE LOVOZERO TUNDRA]: *Trudy Inst. geol. Nauk, Akad. Nauk SSSR*, no. 31, *Min. Geokhim. ser.*, no. 6.
- uiznetsov, V. I., 1947, [THE PROBLEM OF THE ISOMORPHISM OF Ta, Nb, Sn and Ti]: *Mineralog. Sbornik L'vov geol. obshch.*, no. 1.
- anteleyev, P. G., 1938, [THE PROBLEM OF Ti-Nb-Ta IN ALKALIC ROCKS OF ILMEN MT., URALS]: *Izvest. Akad. Nauk SSSR*, no. 5/6.
- ankama, K., 1944, [THE GEOCHEMISTRY OF TANTALUM]: *Bull. comm. geol. Finlande*, no. 133.
- \_\_\_\_\_, 1947, [ON THE GEOCHEMISTRY OF COLUMBIUM]: *Science* 106, no. 2740.
- Rankama, K., and Sahama, Th. G., 1949, [GEOCHEMISTRY]: Chicago-Helsinki.
- Semenov, E. I., 1956, [KUPLETSKITE, A NEW MINERAL OF THE ASTROPHYLLITE GROUP]: *Doklady Akad. Nauk SSSR*, 108, no. 5.
- \_\_\_\_\_, 1957, [OXIDES AND HYDROUS OXIDES OF TITANIUM AND NIOBIUM IN LOVOZERO ALKALIC MASSIF]: *Trudy Inst. min., geokhim. i kristallokhim. redkikh elementov, Akad. Nauk SSSR*, no. 1.
- Semenov, E. I., and Burova, T. A., 1955, [THE NEW MINERAL LABUNTSOVITE AND THE SO-CALLED TITANO-ELPIDITE]: *Doklady Akad. Nauk SSSR* 101, no. 6.
- Shcherbina, V. V., 1952, [GEOCHEMICAL FEATURES OF THE ELEMENTS IN THE DIAGONAL SERIES OF THE PERIODIC SYSTEM Ti-Nb-W]: *Doklady Akad. Nauk SSSR* 85, no. 4.
- Strunz, H., 1957, [MINERALOGISCHE TABELLEN, Leipzig.
- Tikhonenkov, I. P., Semenov, E. I., and Kazakova, M. E., 1957, [FIRST FIND OF ELPIDITE IN THE UNION]: *Doklady Akad. Nauk SSSR* 114, no. 5.
- Vinogradov, A. P., 1956, [REGULARITIES OF THE DISTRIBUTION OF THE CHEMICAL ELEMENTS IN THE EARTH'S CRUST]: *Geokhimiya*, no. 1.
- Znamensky, E. B., Rodionova, L. M., and Kakhana, M. M., 1957, [THE DISTRIBUTION OF NIOBIUM AND TANTALUM IN GRANITES]: *Geokhimiya*, no. 3.

# THE SALT BALANCE OF THE ARAL SEA<sup>1</sup>

by

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• prepared by Research International Associates •

## ABSTRACT

In the Aral Sea there exists an excess of influx of salts over loss by deposition, yet there has been no appreciable increase in the salinity of the sea since 1871. Loss of water by evaporation is less than influx by drainage, hence influx of ground water cannot explain it. A method for calculating the salt loss from interior basins by wind is described and analyzed mathematically. Only 0.05 percent of the salt carried in by river drainage is lost through the action of wind. Outflow of saline water by filtration through the sandy shores along the coasts is shown to be a factor explaining salt loss and the maintenance of salinity equilibrium. --M. Russell.

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## INTRODUCTION

To solve the problem of the "geographic paradox" of the Aral Sea, the cause of its low salinity, and, in addition, to approximate future changes in its chemical nature, it is necessary to give a quantitative estimate of the elements constituting its salt balance. Calculations of the "age" of the Aral Sea, that is, the time of the formation of its salt mass from salts transported by river drainage, excluding consideration of the salt lost by the sea through the course of time, lead invariably to an underestimation of its geologic age.

To an even greater degree, the deficit of individual components of the salt balance has considerable significance in calculations of the future salt regime of the sea, in connection with the control of river drainage. Earlier ideas on the salt balance of the Aral Sea were, for the most part, of a purely theoretical nature and were not supported by corresponding observations or were based on obsolete materials.

Thus, this author [Blinov, 1947] and Alekin [1947] presented several theoretical ideas on the formation of the salt composition of the Aral Sea, in which the role of eolian influx and loss of continental and marine salts, as well as the role of the *kultiki* and "shoestring" lakes, were examined.

Solovyeva [1950] published an article which examined the dynamics of the salt balance in the Aral Sea in relation to the proposed hydro-technic structure of the Amu-Darya and Syr-Darya basins. But even Solovyeva based her calculations on the influx of salt from rivers and the subsequent change in the hydraulic and

salt balances of the Aral Sea.

In 1952 and 1953, the author published certain calculations on the salt balance of the Aral Sea and possible changes in its salt regime regime resulting from partial elimination of drainage. Alekin also published some theories on the change of the Aral Sea regime in connection with the projected control of the Amu-Darya drainage. In these publications, estimates are given for the changes in average salinity of the Aral Sea under systematic elimination of waters draining into the sea.

In the publications of S. Yu. Geller and R. A. Sorokina [1953] concerning the consequences of the imminent drop in the level of the Aral Sea, the authors have examined not only the future physico-geographic and hydrologic changes in the Aral Sea, but also the economic-geographic significance of these changes. However, it can be said that Geller and Sorokina did not consider the problem of hydraulic and salt balances of the sea. Therefore, they came to paradoxical conclusions which are not realistic.

However, lack of marine investigation and insufficient data on its hydrology, geochemistry, and hydraulic and salt balances did not permit the above-mentioned authors to give a sufficiently complete analysis of the present salt balance of the Aral Sea and to perform the necessary estimates of future changes in its salt regime, after control of drainage into the sea has been effected.

Investigations of the past few years have considerably increased our knowledge of the Aral Sea, and the question of the hydraulic balance of the sea as examined in detail by Samoylenko explains to some degree the nature of the salt balance. It is now also possible to make a quantitative estimate of the salt balance and to perform the necessary projections of future changes in the salt regime of the sea.

First, all possible causes of salt influx and

<sup>1</sup>  
Translated from *Gidrokimiya Aralskogo Morya*, Chapter III, p. 80-104, 1956.



loss as exemplified by specific physico-geographic conditions in the Aral Sea will be examined. For a closed, undrained interior basin such as the Aral Sea, the following states of salt influx and loss are theoretically possible and are actually observed:

#### Salt Influx

1. Salts transported by the river drainage system  $S_r$ .
2. Salts transported by ground-water feeding the sea  $S_{gr}$ .
3. Salts transported by the atmosphere  $S_{atm}$ .

#### Salt Loss

1. Salts lost as a consequence of infiltration of water into the shore and sea bottom  $S_f$ .
2. Salts lost in shoestring bays and in gulfs  $S_{bay}$ .
3. Salts subjected to sedimentation, forming bottom sediments  $S_{sed}$ .
4. Salts lost to the atmosphere by wind action  $S_{wind}$ .

If the change or stability over a period of time of the entire salt mass in the closed watershed depends on salt influx-loss, the average salinity of the water (the average content of salts per unit volume or weight) will also

depend on the hydraulic balance of the water reservoir, that is, on the changes in the volume of the water as in

$$V_0 S_0 = V_1 S_1. \quad (1)$$

With the increase in volume due to influx of water not containing salt, the salinity is correspondingly decreased and, conversely, with the increase of evaporation over influx of water and the decrease of volume, the salinity is increased proportionally to this decrease. As far back as 1908, Berg, and later Nikolsky [1940] and V. S. Romashkin, indicated the close relationship between the average salinity and the sea level and, consequently, the volume of the Aral Sea (tables 33 and 34).<sup>2</sup>

TABLE 33. Level and salinity of the Aral Sea (after Nikolsky)

Year	1873	1900	1931
Level (average, in meters)	49.5	50.5	52.0
Salinity (‰)	10.9	10.4	10.2

Romashkin, in processing data of prolonged salinity and sea-level readings at certain hydrometeorologic stations located along the coast of the Aral Sea, noted a marked relationship between the average annual sea level and the average salinity of the surface sea waters (table 34). The relationship between average salinity and the elevation of sea level for three hydrometeorologic

TABLE 34. Average salinity of surface waters in the Aral Sea and the average annual level for hydrometeorologic stations at the Aral Sea, Vozrozhdeniya Island, and Uzun-kari (after Romashkin).

Year	Aral Sea		Vozrozhdeniya Island		Uzun-kari	
	Level along depth gauge (cm)	Salinity (‰)	Level along depth gauge (cm)	Salinity (‰)	Level along depth gauge (cm)	Salinity (‰)
1942	129	10.14	128	10.21	130	11.29
1943	138	9.17	134	9.51	139	9.91
1944	130	10.54	128	9.96	129	11.27
1945	137	9.54	no data		132	11.27
1946	152	9.03	146	9.51	147	10.25

<sup>2</sup> Table and figure numbers are here the same as in the original Russian work.--M.R.

stations (table 33) is also represented in Figure 13.

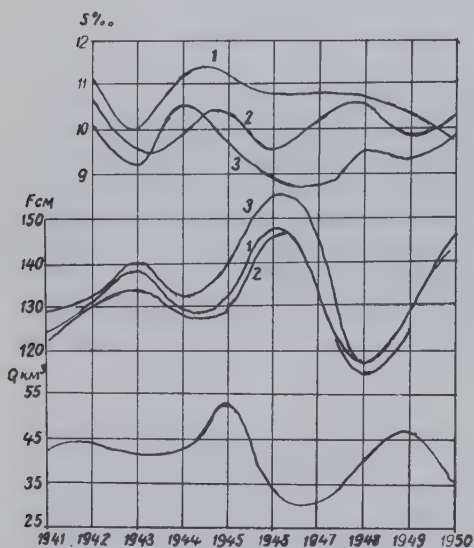


FIGURE 13. The relationship between average annual salinity (‰) and average annual sea level (F) from observations at hydrometeorologic stations at Uzun-kari (1), Vozrozhdeniya Island (2), and the Aral Sea (3) for the period between 1941 and 1950. At the bottom—curve for the changes in average annual flow (Q) of the Amu-Darya for the same period.

Insofar as the level and, consequently, the volume of the sea depends on the amount of river-water influx, a decrease in the flow of water should result in a drop in sea level and a corresponding increase in the average salinity of the Aral waters. Thus, it follows that, on the basis of formula (1) and the components of the sea's salt balance, the average salinity ( $S_t$ ) after  $t$  years, beginning with a systematic decrease in the influx of water, with the initial volume of the sea ( $V_0$ ) changed to volume ( $V_t$ ), can be expressed by the formula

$$V_t S_t = V_0 S_0 + V_r (S_r - S_{sed}) + V_{gr} S_{gr} + V_{atm} S_{atm} - (V_f S_f + V_{wind} S_{wind} + V_{bay} S_{bay}), \quad (2)$$

where  $V_t$  and  $S_t$  are the volume and salinity of the sea after  $t$  years beginning with the elimination of part of the water influx,  $V_0$  and  $S_0$  are the initial volume and salinity of the sea,  $V_r$  and  $S_r$  are the volume and salinity of the river waters entering the sea during  $t$  years beginning with the elimination of part of the influx minus the salts precipitated on the sea bottom ( $S_{sed}$ ),  $V_{gr}$  and  $S_{gr}$  are the volume and salinity of ground water flowing into the sea during  $t$  years beginning with the decrease in

water influx,  $V_{atm}$  and  $S_{atm}$  are the volume and salinity of atmospheric sediments deposited during  $t$  years beginning with the decrease of water influx,  $V_f$  and  $S_f$  are the volume and salinity of water filtered into shore and sea-bottom sediments during  $t$  years,  $V_{bay}$  and  $S_{bay}$  are the volume and salinity remaining in shoestring bays and gulfs,  $V_{wind}$  and  $S_{wind}$  are the volume and salinity of water carried into the atmosphere by wind action.

For the solution of the problem of the future salt regime of the Aral Sea, it is obviously necessary to quantitatively estimate each of the factors controlling the salt and hydraulic balances, both under existing and future conditions of water influx. All the factors controlling the salt balance in the Aral Sea will be examined in turn; quantitative estimates will be attempted. At present, not all components of the salt balance can be accurately determined from direct observation. In certain cases, only an indirect approach can be employed. Among factors which can be estimated only indirectly are ground-water influx, filtration, and salt lost by the sea in bays and gulfs as a result of changes in sea level.

#### FACTORS CONTROLLING THE EFFECTS OF INFLUX ON THE SALT BALANCE

##### River Drainage

The most reliable values for salt influx into the Aral Sea have been obtained at the Amu-Darya and Syr-Darya rivers. Here, observations on the rate of flow, salt composition, and the amount of suspended particles draining into the Aral have been made for a sufficiently long period of time. Data from these observations have been processed and published by Alekin [1949] and K. M. Stepanova [1948].

Prolonged, detailed studies of the salt influx from rivers have been made by Alekin who used data on the rate of flow and composition of ions dissolved in waters of the Amu-Darya at Chatla village and of the Syr-Darya at Begovat village (tables 35 and 36). The average salt influx from the Amu-Darya at Chatla village for a period of several years, according to Alekin, is 18.9 million tons per year and for the Syr-Darya at Begovat village, 6.05 million tons per year (tables 37 and 38).

Actually, the salt influx from the Amu-Darya is smaller than the amounts measured at Chatla village (table 35) because part of the river water is lost below Chatla in the delta and does not reach the sea. True values for the salt emptied into the Aral Sea by the Amu-Darya are given in Table 37. The average amount of salt brought to the mouths of the delta by the Amu-Darya, as measured over a period of



L. K. BLINOV

TABLE 35. Average ionic influx of the Amu-Darya at Chatla village for 1913, 1934, 1938, 1945, 1948, and 1949 in milligrams per liter (after Alekin)

Month	Flow (km <sup>3</sup> )	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> +K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Total ions
January	1.64	105.8	16.2	80.5	189.6	154.9	123.8	670.8
February	1.68	106.4	16.2	92.8	189.4	161.4	137.9	704.1
March	1.83	100.8	16.6	112.0	183.4	168.7	154.2	735.7
April	2.36	97.7	16.4	96.2	166.6	166.6	137.6	681.1
May	4.81	95.2	12.3	61.5	169.3	131.6	95.7	565.6
June	7.21	78.3	11.8	25.8	148.3	94.9	53.2	412.3
July	8.94	71.7	8.9	26.0	140.5	79.9	49.4	376.4
August	7.74	68.3	8.6	29.2	138.7	75.2	51.4	371.4
September	4.76	76.0	8.0	22.5	136.4	82.2	49.5	374.6
October	2.88	87.9	8.6	29.8	147.0	94.9	67.3	435.5
November	2.31	94.2	12.9	42.5	159.5	110.9	90.1	510.1
December	2.02	105.2	16.1	69.5	187.6	143.5	116.4	638.3
Average for the year		90.6	12.7	57.4	163.0	122.1	93.9	539.7
Average for the year (suspended in stream)		81.1	11.2	43.3	153.5	104.9	74.7	470.8

TABLE 36. Average ionic influx of the Syr-Darya at Begovat village for 1937 to 1944 in milligrams per liter (after Alekin)

Month	Flow (km <sup>3</sup> )	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> +K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Total ions
January	0.81	101.5	31.4	40.8	214.6	210.4	50.1	648.8
February	0.83	113.5	33.6	167.5	198.8	300.9	65.5	879.8
March	1.16	111.1	34.8	73.0	202.9	299.2	64.9	785.9
April	1.34	104.3	25.6	58.5	196.0	221.9	65.1	671.4
May	1.51	76.8	18.2	25.7	180.0	119.2	29.3	449.2
June	1.48	66.0	12.7	16.3	169.8	91.6	18.9	365.3*
July	1.50	67.9	12.7	20.7	151.8	98.5	29.8	375.4*
August	1.18	68.5	12.0	27.1	170.3	94.2	27.8	399.9
September	0.86	90.1	16.1	32.6	212.2	127.8	38.4	517.5*
October	0.91	82.3	18.8	37.2	180.5	150.4	39.6	508.8
November	0.98	92.7	17.2	40.7	199.7	166.9	37.9	555.1
December	0.93	103.1	24.4	30.7	208.9	181.6	41.3	590.0
Average for the year		89.8	21.4	47.6	189.6	171.9	42.0	562.3
Average for the year (suspended in stream)		87.6	20.4	43.8	186.1	164.4	40.3	542.8

\* [Data for 3 months are questioned; sum of parts shown gives Totals of 375.3 (June), 381.4 (July) and 517.2 (Sept.). --Ed]

TABLE 37. Average annual ionic influx from the Amu-Darya in thousands of tons (after Alekin)

Water flow (km <sup>3</sup> )	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup> +K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>-</sup>	Total ions
From observations at Chatla village							
48.09	3,998.0	537.5	2,089.0	3,630.0	5,052.0	3,593.0	18,909.0
Flow into the sea with allowance for the loss at various deltas							
42.00	3,378.8	573.8	2,418.5	4,157.9	3,905.8	3,308.0	17,742.8

several years, is, according to Alekin, 17.74 million tons per year (table 37). Loss of water by the Syr-Darya in its delta is quite small; therefore, the measurements taken at Begovat can be used without correction. This amount averages 6.05 million tons per year, as measured over a period of several years (table 38). Therefore, the average annual salt influx from the rivers feeding the Aral Sea is: from the Amu-Darya, 17.74 million tons; from the Syr-Darya, 6.05 million tons; the total, 23.79 million tons.

Comparison of the amount of salts brought in and the total salt mass of the Aral Sea leads to conclusions which, at first, seem to be paradoxical. As the average salinity is 10.3 ‰ [parts per thousand], the salt mass of the sea is 10.53 milliard (billion) tons. In other words, the annual influx of salts equals 1/422 part of all the salts in the sea. Therefore, if no salt is lost, the salt mass could have been formed from river drainage in 422 years (it has been mentioned above in Chapter I that Berg, obtaining his figures by analogous calculations, determined the "age" of the Aral Sea to be 320 years). It is obvious that an "age" of 422 years, that is, the time necessary for the formation of its salt mass from river salts, cannot be accepted. According to geologic data, the age of the sea is irreconcilable with the "age" as calculated from the rate of salt influx from rivers.

Obviously, salt loss must also occur in the salt balance of the sea. One of the main factors in the salt loss is chemical and biochemical precipitation of matter brought in by river drainage. It is well known that river waters are rich in easily precipitated soluble carbonates of alkali-earth metals, primarily calcium. The Aral Sea is not only saturated, but even supersaturated, with calcium carbonate. Thus, carbonates brought to the sea by rivers should be completely precipitated. As a matter of fact, as has been shown by observations made by Zenkovich [1947] and Brodska [1949, 1952], 64.2 percent of the sea bottom is covered by a gray mud containing up to 69 percent calcium carbonate, primarily of chemogenic origin.

Microscopic investigations by Zenkovich and Brodska indicate that 60 to 70 percent of the  $\text{CaCO}_3$  in the bottom sediments was formed through chemical precipitation and only 40 to 30 percent by biological processes. From this it may be assumed that calcium carbonate brought to the sea by river drainage is completely precipitated.

On the basis of the average amount of ions brought by river drainage into the Aral Sea (table 39), it is not difficult to calculate the amount of calcium carbonate deposited annually and the amount of salts remaining in solution in the sea.

A theoretical calculation of calcium carbonate precipitation in the Aral Sea according to its solubility product, as has been adopted in chemical laboratory practice, is, in this instance, impossible from a practical point of view. For such a complex mixture of electrolytes as is the water of the Aral Sea, the solubility products would differ considerably from those usually contained in texts on analytical chemistry. As can be expected, the solubility product of calcium carbonate in the presence of neutral salts is considerably higher than the thermodynamic solubility product of  $\text{CaCO}_3$  in pure solution. According to Koltzof and Sendell [1938],  $\text{SP}_{\text{CaCO}_3} = 1.2 \times 10^{-8}$ ; according to Frir and Johnson [1929],  $\text{SP}_{\text{CaCO}_3} = 4.82 \times 10^{-9}$ . Moberg [Bruyevich, 1937] and others have accepted the value  $\text{SP}_{\text{CaCO}_3} = 2.4 \times 10^{-6}$  for

oceanic waters having normal salinity. If the values for the activity coefficient determined by Moberg are introduced ( $\text{CO}_3^{2-}$  [Tr.: should be either  $\text{HCO}_3^-$  or  $\text{CO}_3^{2-}$ ] ion=0.015 and Ca ion=0.14), the solubility product for sea water approaches the value indicated by Frir and Johnson.

However, the solubility product for  $\text{CaCO}_3$  in the water of the Aral Sea cannot as yet be determined with sufficient certainty and accuracy. Such an undertaking would necessitate separate experimental investigations.

TABLE 38. Average annual ionic influx from the Syr-Darya in thousands of tons (after Alekin)

Water flow (km <sup>3</sup> )	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+ + \text{K}^+$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	Total ions
13.5	1,182.7	278.1	591.5	1,235.3	2,219.0	544.2	6,050.8

TABLE 39. Average ionic flow of the Amu-Darya and the Syr-Darya rivers for a prolonged period of time in milligrams per liter (after Alekin)

River	$\text{Ca}^{2+}$	$\text{Mg}^{2+}$	$\text{Na}^+ + \text{K}^+$	$\text{HCO}_3^-$	$\text{SO}_4^{2-}$	$\text{Cl}^-$	Total ions
Amu-Darya	83.1	11.12	43.4	153.5	104.9	74.1	470.8
Syr-Darya	87.6	20.6	43.8	186.1	164.4	40.3	543.8



It is much more simple and certain to make such calculations with the assumption that the water of the Aral Sea is already supersaturated with calcium carbonate, as was shown by Fedosov [1950] and us, and also as indicated by isothermal evaporation of Aral waters described above.

As a consequence of the supersaturated state of the Aral Sea with respect to calcium carbonate, any calcium brought to the sea via river drainage should, without fail, enter the solid phase [Tr.: as  $\text{CaCO}_3$ ], precipitated from solution.

On the basis of average composition of river water given in Table 39, the following has been found:

For the Amu-Darya River	
$\text{HCO}_3^-$ is completely precipitated	153.5 milligrams/liter or 32.5 percent of total salts
$\text{Ca}^{2+}$ is precipitated in amounts equivalent to the amount of $\text{HCO}_3^-$	50.3 milligrams/liter or 10.7 percent of total salts
Total	203.8 milligrams/liter or 43.2 percent of total salts

For the Syr-Darya River	
$\text{HCO}_3^-$ is completely precipitated	186.1 milligrams/liter or 34.3 percent of total salts
$\text{Ca}^{2+}$ is precipitated in amounts equivalent to the amount of $\text{HCO}_3^-$	61.0 milligrams/liter or 11.2 percent of total salts
Total	247.1 milligrams/liter or 45.5 percent of total salts

Using the values for the average annual influx of salt into the Aral Sea from river drainage (tables 37 and 38), it is quite simple to determine the average amount of salts brought in by river drainage and how much enters the salt mass of the sea and how much enters the solid phase as bottom sediment (table 40).

TABLE 40. Average annual amount of salt transported by river drainage to the Aral Sea for salts remaining in solution are those precipitated

River	Amount of salt in millions of tons		
	Annual influx	Remaining in solution	Precipitated
Amu-Darya	17.74	10.10	7.64
Syr-Darya	6.05	2.75	3.30
Total	23.79	12.85	10.94

If the precipitation of calcium carbonate is considered, the amount of salt brought annually to the Aral Sea by drainage which enters the salt mass (12.85 million tons) constitutes 1/819 of the total salts in the sea water. In other words, in the presence of calcium carbonate precipitation, all the salt mass of the sea could have been formed by river drainage in 820 years; the annual increase in average salinity would be 0.012‰. Obviously, this length of time for the formation of the Aral salt mass does not agree with geologic theories on the age of the Aral Sea either. Moreover, supposing that the average annual increase in salinity is 0.012‰, the average salinity of the sea during the last 80 years, from the time of the first chemical investigations (1871), should have increased by 1‰, which could hardly have been left unnoticed by contemporary investigators. Observations made during this 80-year period indicate that there has been no gradual increase in the salinity of the sea. As has been noted before, observed changes in salinity are not gradual but periodic; they depend on changes in sea level. The relative stability in the average salinity of the sea in time indicates that, besides precipitation as sediments, other means of salt loss exist in the salt balance of the sea--these will be examined below.

#### Underground Influx

The second possible source of salt influx into the Aral Sea may be highly mineralized ground water. The only investigation devoted especially to this problem has been Zaykov's work on the inflow of ground water [1946].

Obviously, considerable influx of ground water, both highly mineralized and fresh, should result in a corresponding anomaly in the distribution of salinity at the places of influx. However, measurements of salinity along the bottom did not indicate any anomalies or disturbances in the general pattern of salinity changes which were caused solely by hydrologic means. Moreover, the study of the hydraulic balance in the sea indicates the converse: loss of water by evaporation is less than influx of water by drainage. Consequently, the influx of ground water should be eliminated as a factor in the hydraulic balance of the sea. In order to maintain equilibrium in sea level, there should be loss through infiltration of water along the shore and bottom rather than influx of ground water. Finally, even such a major and quantitatively well-defined factor contributing to salt influx as river drainage seems to have little effect on the change in salinity of the sea. It is difficult to admit that the influx of salt from ground water should have a greater or equal value to salt influx from river drainage. Therefore, the factor  $V_{gr}S_{gr}$  in formula (2) can be considered equal to 0.

Influx of Salt From the Atmosphere

In geochemical literature there are indications that certain intracontinental basins contain salts transported from oceans and seas by prevailing winds. Classic examples of this are the Indian lakes Sambkhar and Rajputan (described by F. Clark [1924]) which are located in the monsoon belt 400 miles from the sea. According to Clark, the basin of one of these lakes receives 3,000 tons of salt annually from the atmosphere; the basin of the other lake receives 1,300 tons. The author [1950, 1951] presented several ideas on the role of oceans and seas in salt deposition over soil and water of land areas, especially the extensive territories of Kazakhstan and central Asia. The salt is transported from marine reservoirs by means of mechanical evaporation and wind action.

In this paper, we will only consider that salt from the atmosphere which falls directly on the sea surface as that entering the salt balance as the factor  $V_{atm}S_{atm}$  in formula (2), because those salts coming originally from the atmosphere to the sea basin via primary deposition on land are partially washed in with thaw-waters, torrential rains, and river waters; therefore, these cannot be differentiated in the salt balance.

Influx of salt from the atmosphere can occur through eolian transportation of salt in solid form from salt marshes and soils of the area surrounding the Aral Sea, by settling of solid, finely dispersed salt particles transported from marine basins under corresponding conditions of atmospheric circulation, or from precipitation falling on the surface of the sea. No observations on the influx of salt from the atmosphere in solid or liquid form had been made prior to 1951. During the 1951-1953 expedition, the author observed the dust content of air over marine basins, the amount of solid-salt dispersions, and the salt content of precipitation falling directly on the open sea and coastal zones. These observations were made according to a method developed and applied by the author in analogous work in the Caspian Sea area in 1947-1948. The method is described in detail in a previously published paper; consequently, the methods used will be described only briefly here.

Measurements of the dust content of the air were made with an Owens dust meter, as well as by the aerodispersion settling method on a glass plate; air dispersions were later analyzed microscopically and chemically. Chemical analyses of the sediments involved the micropotentiometric method for chlorides and the micronephelometric method for sulfates. Total salt contained in the sediments was calculated by multiplying the amount of chloride contained in the sample

(milligrams per liter) by a corresponding conversion factor (2.84). This method of determining the total salt content gave only an approximate value for the mineralization of atmospheric water, but for our purposes, the calculation of the salt balance, the method was quite satisfactory. Due to the working conditions of the expedition and the task set before it, we did not have the opportunity to employ a more thorough method and increase the number of components determined.

Microscopic studies of aerodispersion settling in various parts of the Aral basin and under various wind velocities indicated a complete absence of terrigenous particles for almost all of the area. Only in a narrow coastal belt of the eastern seacoast, no more than 3 to 5 kilometers from the shore, during relatively strong north-east and east winds was it possible to observe the presence of terrigenous particles in the samples, which were obtained by either the Owens or settling methods. The atmosphere of the entire central sea area under observation was completely free of terrigenous particles. These observations were made during the spring-summer period which is the season of weakest winds. Therefore, of course, we do not exclude the possibility of dust storms during periods of stronger winds and the presence of dust particles in the atmosphere of the central part of the sea. Such phenomena can only be episodic, occurring for the most part during the cold part of the year; they cannot have any great significance in the salt balance of the sea. The wind has greater significance in the salt balance as an agent of salt loss. This question will be discussed in greater detail in the following section.

The influx of salt from the atmosphere sediment cannot have any great importance in comparison with the salt influx due to river drainage. As has been determined by Zaykov [1946] and Samoylenko, the amount of sediment settling on the surface of the sea is very small; it averages approximately 5.4 cubic kilometers or approximately 10 percent of the amount brought in by river drainage.

Studies on the salt composition of the precipitation falling directly on the Aral Sea are very few, mainly because precipitation here is very rare, particularly during the warmer part of the year. During the period of experimental work (1951-1953), we were able to observe rainfall in the basin and to collect samples for study: in June 1951, in the city of Aralsk and, in July 1953, at sea in the vicinity of Tokmak-Ata Island and between Muynak and Uyala islands. The collected samples were examined for chloride and sulfate content. From these data the approximate salt content was calculated (table 41).

If we assume that the average salt content



TABLE 41. Chloride and sulfate content in milligrams per liter in precipitation falling on the surface of the Aral Sea

Date of observation	Chlorides	Sulfates	Sulfates/Chlorides	Calculated total salts
June 30, 1951	1.05	1.23	1.17	2.98
July 25, 1953	5.83	6.20	1.06	16.56
July 25, 1953	5.50	6.20	1.13	15.62
Average	4.13	4.54	1.12	11.72

in the sediment falling on the surface of the sea is approximately 120 milligrams per liter and that the average annual amount of sediment is 5.4 cubic kilometers, the total influx of salt with the sediment amounts to 64.8 thousand tons per year or approximately 0.005 percent of the total amount of salt brought in annually by drainage. It is obvious that precipitation and fine solid dispersions of salt falling directly on the sea do not play a significant role in the salt balance of the Aral Sea or in our calculations of its future salt regime under controlled drainage conditions.

Let us now consider the salt loss in the salt balance of the sea.

The Aral Sea does not have any visible surface effluence. If, as is indicated by the disagreement in the above calculations, salt loss does not occur, a gradual increase in salinity due to influx of salt from river drainage would be unavoidable. But the increase has not actually been observed. It is obvious that the problems posed 50 years ago by Berg on the cause of the low salinity of the Aral Sea and on the quantitative estimate of salt loss represent considerable difficulties; for this reason, the problems have not been adequately resolved during the last 50 years. The solution of these problems is possible only with a quantitative evaluation of all the possible factors which may retard the salting of the sea, no matter how insignificant they may seem at first glance from the qualitative evaluation. Moreover, an evaluation of these factors is necessary for the study of other areas analogous in physico-geographic environments, hydrology and climatology to those of the Aral Sea.

#### FACTORS EFFECTING THE LOSS OF SALT IN THE SALT BALANCE

##### Loss of Salt Through Wind Action

It has been known for a long time that wind is not only a factor in the physical evaporation of sea water, facilitating and accelerating the transformation of water into vapor, but that it also acts mechanically by carrying droplets and spray into the atmosphere from wave crests near the surf zone. N. N. Zubov [1938] has called this phenomenon "mechanical evaporation" as distinguished from physical evaporation, which accomplishes transformation of

water from one aggregate state to another. The smallest particles of sea water carried off by the wind evaporate in the air stream. The finely dispersed solid particles of salt resulting from this evaporation are carried by wind and convection currents of air for considerable distances from the shoreline both horizontally and vertically. These particles may form nuclei for cloud structures or may settle on continental soils under favorable conditions of atmospheric circulation. Quantitative estimates of salt loss from marine basins through wind action have been made only quite recently by S. V. Dobroklonsky and P. G. Vavilov [1938], by the author [1950], and by R. I. Grabovsky [1951].

In 1951-1953, eolian salt loss from the Aral Sea was observed by the same means as have already been described for the study of a salt stream directed from the sea into the atmosphere by wind action. The amount of salt contained in sea air was determined with the aid of a special automatic self-catching filter; the linear dimensions and particle structure were determined by microscopic study of salt specks on glass slides which had been exposed to the salt stream. The content of salt in the atmosphere under various wind velocities at different times and localities is given in Table 42.

As can be seen from Table 42, the absolute content of salt is quite small; it amounts to tenths and hundredths of a milligram per cubic meter of air. However, if we consider the size of the basin, the velocity of the wind, and the duration of its activity, the amount of salt carried into the atmosphere from the sea surface can be considerable. Several methods have been proposed to calculate this amount (Blinov [1950], L. S. Borishansky and Ye. N. Teverovskiy [1952], Grabovsky [1951]). We shall examine the first two methods; these are best suited for our calculations. Grabovsky's method has been developed for oceanic conditions and, thus, is not applicable.

The method suggested by the author is based on the following ideas. Particles torn from the sea surface by the wind will both be supported by turbulent air currents and tend to fall due to the pull of gravity. If in a certain air layer  $z$  the content of salt particles is equal to a certain value  $q$ , the entire salt stream moving upwards can be expressed by the formula

$$Q = -A \frac{dq}{dz}, \quad (3)$$

# INTERNATIONAL GEOLOGY REVIEW

TABLE 42. Observed chloride content and estimated amount of salt dispersed over the Aral Sea in milligrams per cubic meter of air

Date of observation	Coordinates		Wind		Detected chlorine content	Calculated total salt content
	N	E	Direction	Velocity (m/sec)		
	o ' "	o ' "				
June 28	46 41	61 63	-	none	0.008	0.023
June 28	46 28	61 16	SW	4.9	0.018	0.051
June 28	46 08	60 02	NW	5.0	0.021	0.060
June 29	45 45	59 54	N	1.9	0.006	0.017
June 29	45 45	59 30	WSW	1.7	0.009	0.026
June 29	45 45	59 10	W	3.3	0.012	0.034
June 30	45 45	58 50	-	none	0.000	0.000
June 30	45 07	58 41	W	2.5	0.009	0.026
July 1	45 48	58 40	NE	3.9	0.018	0.051
July 2	43 45	59 08	SSW	5.3	0.031	0.088
July 2	44 00	59 30	SE	6.0	0.032	0.091
July 2	44 11	60 00	SE	6.0	0.038	0.108
July 2	44 00	60 29	SE	7.9	0.047	0.133
July 8	45 01	61 07	WNW	10.4	0.073	0.207
July 8	45 45	60 51	SW	7.4	0.085	0.241
July 4	45 56	60 51	SW	7.6	0.111	0.315
July 4	46 06	60 56	WSW	7.8	0.128	0.364
July 4	46 01	60 32	SW	0.9	0.010	0.028
July 19	46 28	61 16	SW	7.6	0.085	0.241
July 19	46 26	61 04	SW	7.9	0.079	0.224

where A is some coefficient dependent upon the velocity of the wind and the roughness of the underlying surface. The stream directed downwards will be equal to  $cq$ , where  $c$  is the rate of particle settling, which is dependent upon particle radius and density.

It is apparent that, at some point, both streams--the one directed upwards and carried by the turbulent air stream and the one directed downwards as a result of particle settling in the field of gravity--will attain equilibrium:

$$-A \frac{dq}{dz} = cq, \text{ or } A \frac{dz}{dq} + cq = 0, \quad (4)$$

from which is derived

$$q = q_0 e^{-\frac{c}{A} z}, \quad (5)$$

where  $q_0$  is the content of particles in the air at the level  $z=0$ . Thus, the distribution of particles carried away by the wind will follow the exponential law, that is, with the increase in the arithmetic progression, the content of salt particles in air will decrease in geometric progression.

If the values  $q_0$ ,  $c$ , and A are known, the total content of salt  $Q$  in the air column over the marine basin can be calculated from the formula

$$Q = q_0 \int_0^{\infty} e^{-\frac{c}{A} z} dz. \quad (6)$$

The salt content of the atmosphere, determining the value  $q_0$ , can be obtained from direct determinations using the method described above. The selection of values for  $c$  and A presents considerable difficulties. In the first place, the linear dimensions of the particles, as observed, change in the air stream due to drying of the water droplets, which is, in turn, dependent on the temperature and humidity of the air. The temperature and humidity also change, both horizontally and vertically. The selection of values for A is also quite difficult due to the intermittent winds and the nature of the underlying surface.

Borishansky and Teverovsky [1952], on the basis of experimental data collected by the author, have proposed a different method of calculating the amount of salt entering the atmosphere from the sea by means of wind action. Borishansky and Teverovsky base their calculations on the following concepts. The concentration of matter carried into the atmosphere can be calculated by the diffusion equation:

$$\frac{dc}{dt} + u \frac{dc}{dx} = \frac{d}{dx} (D_x \frac{dc}{dx}) + \frac{d}{dy} (D_y \frac{dc}{dy}) + \frac{d}{dz} (D_z \frac{dc}{dz}), \quad (7)$$

where  $c$  is the weight concentration of the "mixture" (the authors consider the salt particles in sea air as a "mixture", without consideration of their physicochemical nature or of change within the salt stream);  $x$  is a coordinate lying in the average direction of the wind;  $y$  is a coordinate oriented perpendicular to the wind;  $z$  is a coordinate oriented upwards;  $u$  is the average velocity of the wind;  $D_x$ ,  $D_y$ , and  $D_z$  are



component coefficients of turbulent diffusion along the axes of the coordinates.

In an air stream that has come to rest

$$\frac{dc}{dt} = 0. \quad (8)$$

Teverovsky has shown that concentration of a mixture at various distances from an infinite linear source can be calculated according to the following formula, obtained from the solution of formula (4)

$$c = \frac{Qz_1}{\pi^{1/2} D_z x} e^{-z^2 \frac{u_1^2 z_1^2}{D_z x^2}}, \quad (9)$$

where  $Q$  is the loss from the source in grams per liter front per second,  $u_1$  is the velocity of the wind at an elevation of  $z_1 = 1m$ ,  $z$  is the elevation at which the concentration of salt is being determined.

D. L. Laykhtman [1919] determined the vertical coefficient of turbulent diffusion as being equal to

$$D_z = \frac{0.1444u_1 z}{\ln \frac{z_1}{z_0}}, \quad (10)$$

where  $z_0$  is the roughness of the surface.

Nature of the surface	Roughness (cm)	$D_{z_1}$
Thick snow cover	0.05	0.02
Average uneven snow cover	1.0	0.031
Weak friable snow	2.0	0.037
Bare soil	1.0	0.031
Field, fallow	2.0	0.037
Field, grass-covered	3.0	0.041
Field, wheat-covered	5.0	0.048

If we consider the concentration of particles on the ground as  $z = z_1$ , equation (6) can be written as

$$c = \frac{Qz_1}{\pi^{1/2} D_{z_1} x}, \quad (11)$$

from which we obtain

$$Q = \pi^{1/2} D_{z_1} \frac{x}{z_1} c. \quad (12)$$

If for beach sands we used the values estab-

lished for bare soil, that is  $z_0 = 1$  cm and  $D_{z_1} = 0.031$  and the distance from the source as  $x = 600$  meters (the content of particles in the air was measured at a distance of 600 meters from the shoreline where, as has been determined from observation, the amount of salt in the air is greatest), and substitute these values in formula (9), we get:

$$Q = 1.77 \cdot 0.031 u_1 z_1 \frac{600}{z_1} c = 33 u_1 c. \quad (13)$$

Borishansky and Teverovsky consider that salt concentration increases with wind velocity in the following linear relationship:

$$c = 0.02 \cdot 10^{-3} u_1 (g/m^3). \quad (14)$$

Substituting this value of  $c$  in equation (10), we obtain for the given conditions:

$$Q = 0.66 \cdot 10^{-3} u_1^2 (g/m \cdot sec). \quad (15)$$

Using the above formula and salt-content values for the atmosphere above the Aral Sea and its shoreline obtained from observation (table 42) with average annual data of wind velocity and frequency along eight rhumb lines gathered over a prolonged period of time, we can calculate the average salt loss from the sea due to wind action along each of the rhumb lines.

As the length of the linear source, we use the diameter of a circle equal in area to that of the marine basin. In calculating the average annual amount of salt we presuppose that during four of the winter months the Aral Sea is completely frozen over; therefore, salt loss from the sea surface due to wind action does not occur.

The results of calculations on the amount of salt loss along numerous rhumbs due to wind action are given in Table 43. Wind transportation of salt from the Aral Sea is also schematically represented in Figure 14. As can be seen from Table 43 and Figure 14, the average velocities of the wind over the Aral Sea are quite small: only approximately 4.5 meters per second. During the winter period, when the winds are strongest, the greater part of the sea surface is covered by ice, and wind loss of salt cannot occur. Thus, the relative amount of salt carried off by the wind is quite small (107 thousand tons) and comprises less than 0.05 percent of the salt carried in by river drainage. Obviously, wind loss of salt does not have any great significance in the salt balance of the Aral Sea from our point of view.

TABLE 43. Average annual salt loss due to wind action (along rhumb lines) from the Aral Sea  
In thousands of tons

Direction of wind (rhumb lines)	Average annual wind velocity (meters/seconds)	Frequency (percent)	Average amount of salt carried off by wind annually in thousands of tons
N	4.8	14.0	14.78
NE	5.3	23.0	26.82
E	5.2	13.0	14.87
SE	4.1	8.0	7.21
S	4.0	6.0	5.28
SW	4.6	9.0	9.11
W	4.8	16.0	16.89
NW	5.0	11.0	12.16
Average	4.7		
Total		100.0	107.12

### Filtration

Thus, neither precipitation nor eolian loss of salts from the Aral Sea can be defined as quantitative factors influencing the low salinity of the Aral Sea. Obviously, there is another, more significant factor influencing the loss of salt in the balance which determines the stability of the sea's salinity. A most likely factor of this type is loss of water by filtration through the sandy shore along the northern, eastern, and southern coasts of the sea.

The existence of filtration is indicated by the physcogeographic environment of the Aral Sea, the geology and morphology of its coasts, its climate and salinity distribution. The multitude of shallow-water lakes along the eastern coast does not have any visible drainage into the sea as they are speparated by more or less

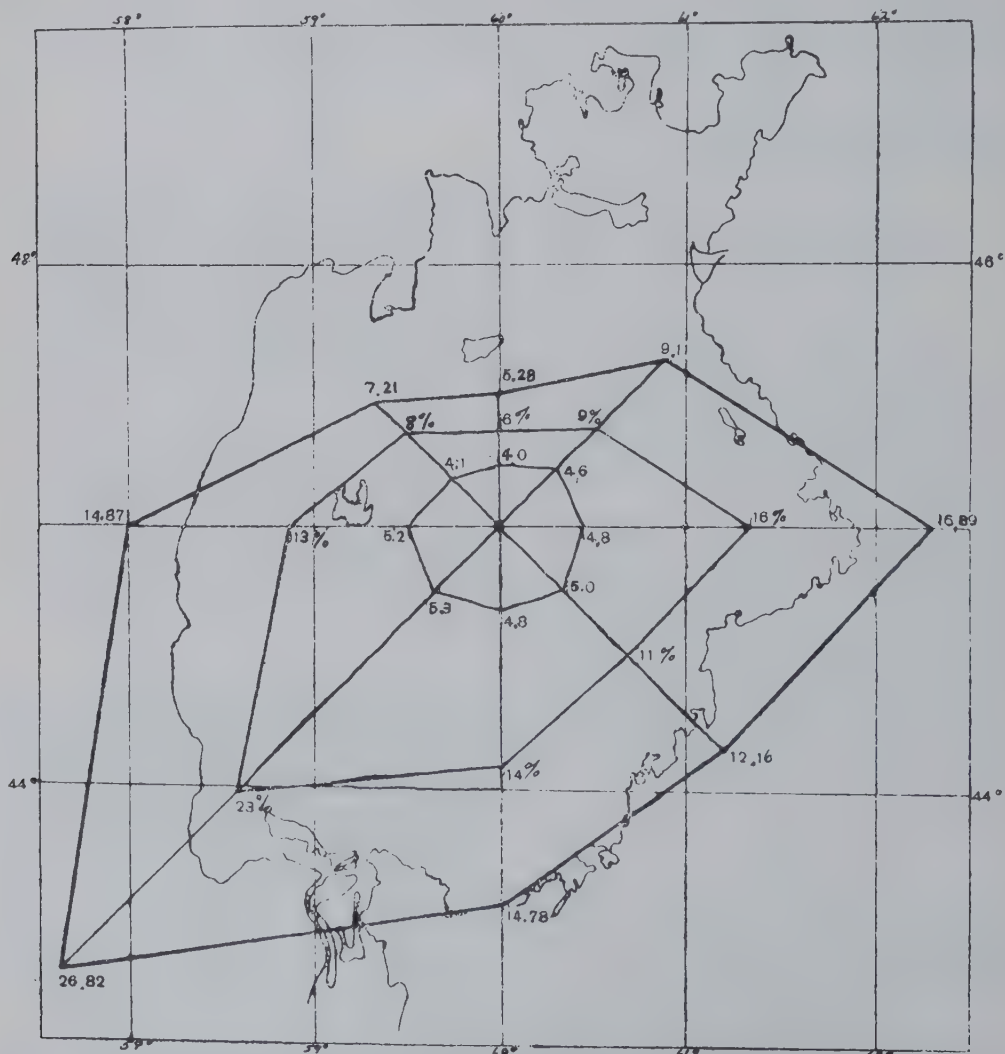


FIGURE 14. Rose of the average annual salt loss due to wind action from the Aral Sea along 8 rhumb lines (in thousands of tons) and roses of the average annual velocity and frequency of winds (percent) along the same rhumb lines



wide sandbars; but they do not dry-up and do maintain a constant level during the entire warm period. The water in these lakes becomes highly saline as autumn approaches, sometimes reaching the saturation point for such salts as sodium sulfate. Nevertheless, these lakes never dry-up completely. Obviously, they are invisibly fed by filtration of sea water through the sandbars. That filtration actually occurs is also supported by calculations of the hydraulic balance. Without the existence of filtration, there would be a considerable discrepancy in the influx and loss of water. Finally, let us remember that the salinity of the Aral Sea has shown no increase over an 80-year period of observation, despite the considerable influx of salt from river drainage.

On the basis of the observed stability of the salinity, the amount of Aral water which should filter out annually to compensate for the amount of water which is brought to the sea by river drainage is estimated. The average annual influx of salt from rivers, with the exception of precipitated salts, is 12.85 million tons. The average salinity of the Aral water is 10.3 ‰. Thus, the volume of Aral water containing 12.85 million tons of salt, that is, an amount equal to an annual salt influx from rivers, is 1.26 cubic kilometers. An annual loss of 1.26 cubic kilometers of water by the sea through filtration, therefore, compensates for the annual influx of salt by river drainage.

Let us express this volume of water in millimeter layers. If we take the area of the basin as equal to 63,000 square kilometers, 1.26 cubic kilometers of Aral water would obviously correspond to a 20 millimeter layer. Thus, the annual loss of a 20 millimeter layer of water through filtration fully compensates for the salt influx from rivers. This indirect determination of the amount of filtration is not only supported by the nature of permeable sandy ground along the eastern seacoast and by calculations of the hydraulic balance, but also serves as a probable explanation for the low salinity of the Aral Sea. The fact that filtration is a significant factor affecting the hydraulic and salt balances of undrained basins situated in desert zones of the temperate belt is also supported in other instances.

Lake Balkhash is very similar to the Aral Sea in several of its physico-geographic and geochemical features. Lake Balkhash is also a shallow lake situated in an undrained watershed in a desert zone; its average depth is 6.13 meters, its maximum depth is 26.5 meters (P. F. Domrachev [1933]), and it has a greater basin area (20,000 square kilometers). It is fed by two major rivers, the Ili and the Karatal, and by several smaller intermittent streams. Mineralization of the lake is heterogeneous: Lowest in the southwestern part where the Ili River enters and highest in the east, at Gurleyuba bend--

5.2 grams per liter (approximately 5.2 ‰). The average mineralization of the lake, according to V. D. Konshin's calculations, is 2.843 grams per liter and, according to B. A. [A. V. ?] Shnitnikov, 3.97 to 4.71 grams per liter.

The salt mass of the lake is approximately 374 million tons, and the annual salt influx from rivers (excluding suspended particles), according to Konshin and Yunusov [1945], is approximately 4.3 to 5.0 million tons. Thus, if all the salts brought in by drainage were added to the salt mass, all the salt content in the lake could have been formed during 75 to 100 years. Shnitnikov [1936] maintains that salts brought in by river drainage increase mineralization by 0.04 percent annually. On this basis, mineralization would reach its present value in 250 to 300 years.

It is quite clear that this figure for the time of formation of the salt mass cannot be accepted either. It is obvious that calculations of the above authors do not consider loss components of the salt balance.

In the literature we find several indications regarding the cause of low salinity in Lake Balkhash. Berg [1903] has called the low salinity of Balkhash water a geographical paradox. L. A. Molchanov [1929] maintains that the amount of mineralization in the lake depends on the hydraulic balance and changes periodically. During an increase in water influx over loss, and an increase in the water level, salt water migrates into the ground and the lake becomes fresher. During those years when the loss of water is greater than the water influx, salinity increases. However, it is clear that such periodic fluctuations could not offset a progressive increase in salinity due to an uninterrupted (even though variable) salt influx from river drainage.

I. I. Kasatkin [1939] proposed that periodic drainage of lake waters in the direction of Betpak-Dal is possible. With an increase in the water level, partial drainage of the lake occurs, and the salinity decreases. However, the relief makes drainage in the direction of Betpak-Dal impossible.

Many investigators--Berg [1903], Molchanov [1929], V. M. Rylov [1933], S. P. Suslov [1947], and others--explain the weak mineralization of Lake Balkhash by its geologic youth. However, it is quite clear that the geologic age of Lake Balkhash is quite higher than the span of time necessary for the formation of its salt mass from river drainage without any salt loss occurring.

If we assume that the bulk of the water drains into the lake from two rivers, the Ili and Karatal which contribute more than 90 percent of surface drainage and which supply 19.140 cubic kilometers (according to 1929 observations) form-

ing a 1,110 millimeter layer per year, that the amount of precipitation on the lake's surface is 4,330 cubic kilometers (Domrachev [1933]), and that evaporation averages 1,150 millimeters per year (Shnitnikov [1936]), the water balance of Lake Balkhash, not considering filtration, would be, according to 1929 data:

	In cubic kilometers	In millimeters per year layer
Influx		
River drainage	19,140	1,110
Precipitation on the surface of sea	4,330	250
Total	23,470	1,360
Loss		
Evaporation from lake surface	19,900	1,150

The influx exceeds the loss by 3,570 cubic kilometers or a 210 millimeter layer. The area of the basin for our calculations in 17,659 square kilometers.

From data obtained during 1941-1947, the average discharge from the Ili River is 469.7 meters per second; the average discharge from the Karatal River is 31.7 cubic kilometers. Considering the flow of the other rivers entering the Balkhash, the hydraulic balance of the lake for this period would be:

	In cubic kilometers	In millimeters per year layer
Influx		
River drainage	17,350	1,010
Precipitation on the surface of sea	3,460	200
Total	20,812	1,210
Loss (not considering filtration)		
Evaporation from lake surface	19,900	1,150

The influx exceeds loss by 0.913 cubic kilometers or 60 millimeters per year layer.

The relative water balance of the lake indicates the existence of another factor of water loss other than evaporation. In the absence of visible drainage of the lake, the only other possible means of loss is filtration.

Let us attempt to estimate the size of the filtrating layer on the basis of the lake's salt balance and the undisputable fact that the aver-

age salinity of the lake (with periodic fluctuations) generally remains constant. Because the area of the basin and its average salinity are subject to constant fluctuations, six variables will be calculated: three values for the water level and areal extent, 17,659, 21,632 and 22,271 square kilometers, and for the values of average salinity (mineralization), 2.84 (Konshin [1945]), 3.97, and 4.71 (Shnitnikov [1936]) grams per liter. In these calculations, it will be assumed that the average annual influx of salt from the Ili and Karatal rivers is 4,802 million tons (table 44).

TABLE 44. Amount of salt (a=thousands of tons) contained in a layer of water 1 centimeter thick with various values for the basin area and average salinity of Lake Balkhash and the value for a layer (b=millimeters) which should filter out annually in order to maintain average salinity constant

Basin area	Average salinity of lake (grams per liter)					
	2.84		3.97		4.71	
	a	b	a	b	a	b
17,659	501	86	400	62	830	52
21,632	614	70	855	51	1,040	42
22,271	640	67	895	48	1,060	41

Thus, the thickness of the water layer which should filter through the bottom and shore during 1 year, in order to maintain the average salinity of the lake, ranges from 86 to 41 millimeters, depending on the initial values for the area of the basin and the salinity used in the calculations.

The excess of influx over evaporation, as has been stated previously, comprises a layer of lake water from 210 to 60 millimeters thick. Therefore, the excess of influx water over evaporation in calculations of the hydraulic balance (without considering filtration) more than covers that amount of water necessary to stabilize the existing salinity of the Balkhash.

In the literature there are several other indications regarding continuous seepage of water into the ground. Thus, P.F. Gorbachev [1933] clearly indicates the existence of underground flow of sea water: for instance, underground flow of sea water in the North Sea—"an underground sea strait"—existing in the poldery of the Haarlem Sea. Such continuous seepage of sea water, according to studies by Tilby and Selder, exist on the peninsula of Florida and along the shore of the Gulf of Mexico. Here, part of the gulf stream passes directly from the gulf to the ocean underneath the peninsula through the water permeable strata of the Vicksburg limestone.

We will not attempt to analyze the problem



of the salt and hydraulic balance in Lake Balkhash. The present work is not concerned with this. The example of Lake Balkhash was used here only as a geographic illustration supporting the concept of filtration as an underestimated factor in the salt and hydraulic balance of the Aral Sea.

## REFERENCES

- Alekin, O. A., 1947, K voprosu o proiskhozhdenii solevogo sostava vody Aralskogo morya [ON THE QUESTION OF THE SOURCE OF THE SALT COMPONENTS OF ARAL SEA WATER]: *Meteorologiya i gidrologiya*, no. 4.
- \_\_\_\_\_, 1948, Gidrokhimicheskaya klassifikatsiya rek SSSR [HYDROCHEMICAL CLASSIFICATION OF RIVERS OF THE U. S. S. R.]: *GGI*, no. 4.
- \_\_\_\_\_, 1948, 1949, Gidrokimiya rek SSSR [HYDROCHEMISTRY OF THE RIVERS OF THE U. S. S. R.]: *GGI*, nos. 10, 15.
- \_\_\_\_\_, 1948, 1954, Obshchaya gidrokimiya [GENERAL HYDROCHEMISTRY]: *Gidrometeoizdat*.
- \_\_\_\_\_, 1954, Khimichesky analiz vod sushi [CHEMICAL ANALYSIS OF WATERS OF EVAPORATION]: *Gidrometeoizdat*.
- Berg, L. S., 1902, K morfologii begerov Aralskogo morya [ON THE MORPHOLOGY OF ARAL SEASHORES]: *Ezhegodnik po geologii i mineralogii Rossii*, vol. 5.
- \_\_\_\_\_, 1905, Usykhaet li srednyaya Aziya? [IS CENTRAL ASIA DRYING UP?]: *RGO*, vol. 12, pages 507-521.
- \_\_\_\_\_, 1908, Aralskoe more [ARAL SEA]: *SPb*.
- \_\_\_\_\_, 1909, Predvaritelnyy otchet ob issledovanii oz. Balkhash letom 1903 g. [PRELIMINARY REPORT ON 1903 SUMMER INVESTIGATIONS OF LAKE BALKHASH]: *RGO*, vol. 40.
- \_\_\_\_\_, 1932, Ob urovnyakh Aralskogo morya [ON ARAL SEA LEVELS]: *Zapiski GGI*, no. 8.
- \_\_\_\_\_, 1932, Ob absolutnoy vysote Aralskogo morya [ON THE ABSOLUTE HEIGHT OF THE ARAL SEA LEVEL]: *Zapiski GGI*, vol. 6.
- \_\_\_\_\_, 1945, Pochvy i vodnye osadochnye porody [SOILS AND WATERS OF SEDIMENTARY ROCKS]: *Pochvovedenie*, nos. 9, 10.
- Blinov, L. K., 1946a, Ob osedanii kolloidnykh i vzhveshennykh chastits v more [ON THE PRECIPITATION OF COLLOIDS AND SUSPENDED PARTICLES IN THE SEA]: *Meteorologiya i gidrologiya*, no. 3.
- Blinov, L. K., 1946b, O nekotorykh zavisimosti mineralnogo sostava rechnoy vody ot gidrologicheskikh faktorov [ON THE RELATION OF MINERAL COMPONENTS OF RIVER WATER TO HYDROLOGICAL FACTORS]: *Meteorologiya i gidrologiya*, no. 6.
- \_\_\_\_\_, 1947a, Mikropotentiometricheskyy metod opredeleniya khloridov v prirodnykh vodakh [THE MICROPOTENTIOMETRIC METHOD OF DETERMINING CHLORIDES IN GROUND WATERS]: *Meteorologiya i gidrologiya*, no. 1.
- \_\_\_\_\_, 1947b, K voprosu o proiskhozhdenii solevogo sostava morskoy vody [ON THE QUESTION OF THE ORIGIN OF SALINE COMPONENTS OF SEA WATER]: *Meteorologiya i gidrologiya*, nos. 4, 7.
- \_\_\_\_\_, 1948, Izmenenie soderzhaniya khlorov v krovi Nereis succinea kak sluchay bioticheskogo ravnovesiya [STUDY OF THE CHLORINE CONTENT IN THE BLOOD OF NEREIS SUCCINEA AS A CASE OF BIOTIC EQUILIBRIUM]: *GOIN*, no. 4, (18).
- \_\_\_\_\_, 1950a, O nekotorykh zakonakh raznitsyazheniya glubinnogo raspredeleniya v more soedineniy azota, fosfora, kremniya, rastvorennoy kisloroda i velichin pH [ON VARIOUS LAWS OF DEEP-SEA DISTRIBUTION OF NITROGEN, PHOSPHOROUS AND SILICON COMPOUNDS, DISSOLVED OXYGEN AND pH VALUES]: *GOIN*, no. 15, (27).
- \_\_\_\_\_, 1950b, O postuplenii morskikh soley v atmosferu i o znachenii vetra v soevom balanse Kaspiskogo morya [ON ENTRY OF SEA SALT INTO THE ATMOSPHERE AND ON KNOWLEDGE OF THE WIND IN RELATION TO THE SALINE BALANCE OF THE CASPIAN SEA]: *GOIN*, no. 15, (27).
- \_\_\_\_\_, 1951, O vliyani morya na zasolenie pochvy i vod sushi [ON THE INFLUENCE OF THE SEA ON SALTING OF SOILS AND WATERS OF EVAPORATION]: *Voprosy geografii*, no. 26.
- Borishansky, L. S., and Teverovskiy, Ye. N., 1952, O vynosie morskikh soley vetrami s morya na sushu [ON THE CARRYING OFF OF SEA SALTS BY WIND WITH THE SEA IN A STATE OF EVAPORATION]: *Meteorologiya i gidrologiya*, no. 4.
- Brodskaya, N. G., 1949, Karbonatobrazovanie v Aralskogo more [CARBONATE FORMATIONS IN THE ARAL SEA]: *AN SSSR, Seriya geologicheskaya*, no. 6.

- Brodskaya, N. G., 1952, Donnye otlozheniya i protsessy osadkobrazovaniya v Aralskom more [DATA ON DEPOSITION AND THE PROCESS OF SEDIMENTATION IN THE ARAL SEA]: Instituta geologicheskikh nauk, vol. 5, Geologicheskaya seriya, no. 57.
- Bruevich, S. F., 1937, Gidrokimiya srednego i yuzhnogo Kaspiya [HYDROCHEMISTRY OF THE CENTRAL AND SOUTHERN CASPIAN]: AN SSSR.
- Dobroklonsky, S. V., and Vavilov, P. G., 1930, K voprosu o vynosе morskikh soley s bruzgami vody [ON THE QUESTION OF THE CARRYING OFF OF SEA SALTS THROUGH SURF]: AN SSSR, Seriya geograficheskaya i geofizicheskaya.
- Dombrachev, P. F., 1933, Obshchy plan roboty Balkhashskoy ekspeditsii 1930-31 g. i ego vpolnenie. Issledovaniya ozer SSSR [GENERAL PROGRAM OF THE 1930-31 BALKHASH EXPEDITION AND ITS FINDINGS. RESEARCH ON LAKES OF THE U. S. S. R.]: Gidrometeoizdat, vol. 4.
- Feodosov, M. V., 1950, Novye dannye o gidrokhimii Aralskogo morya. Materialy po ikhtofaune i rezhimu vod Aralskogo morya [NEW DATA ON THE HYDROCHEMISTRY OF THE ARAL SEA. CONTRIBUTIONS ON ICHTHYOFAUNA IN THE HABITAT OF WATER OF THE ARAL SEA]: MOIP, Moscow.
- Geller, S. Yu., and Sorkina, R. A., 1933, K voprosu o posledstviyakh predstoyashchego ponizheniya urovnya Aralskogo morya [ON THE QUESTION OF CONSEQUENCES OF THE IMPENDING DROP IN THE ARAL SEA LEVEL]: AN SSSR, Seriya geograficheskaya, no. 1, page 3.
- Gorbachev, P. F., 1933, Podzemnye tekhniki morskoy vody [UNDERGROUND FLOW OF SEA WATER]: 1-go Vsesoyuznogo gidrogeologicheskogo s'yezda, Coll. 6, Moscow.
- Grabovsky, R. I., 1951, O kontsentratsii khlorida v osadkakh i obachnykh elementakh [ON CONCENTRATIONS OF CHLORIDES IN SEDIMENTS AND REGIONAL FACTORS]: Vestnik, Leningradskogo Universiteta, no. 10.
- Kasatkin, I. I., 1939, Nekotorye soobrazheniya po povody oz. Balkhash [SOME COLLECTED WORKS REGARDING LAKE BALKHASH]: Problem fizicheskoy geografii, vol. 7.
- Koltgof, I. M., and Sendel, E. B., 1948, Kolichestvennyy analiz [QUANTITATIVE ANALYSIS]: Goskhimizdat, M. - L., 1948.
- Konshin, V. D., 1945, Metamorfizatsiya vody oz. Balkhash [METAMORPHISM OF THE WATER OF LAKE BALKHASH]: DAN, vol. 48, no. 5.
- Laukhtman, D. L., and Chudnovsky, A. F., 1949, Fizika prizemnogo sloya [PHYSICS OF EARTH LAYERS]: GTTI, Moscow.
- Molchanov, L. A., 1921, Ozera sredney Azii [LAKES OF CENTRAL ASIA]: Sredneaziatskogo gosudarstvennogo universiteta, Seriya 12-a, Geografiya, no. 3.
- Nikolsky, G. V., 1940, Ryby Aralskogo morya. Materialy k poznaniyu fauny i flory SSSR [FISH OF THE ARAL SEA. CONTRIBUTIONS TO INFORMATION ON FAUNA AND FLORA OF THE U. S. S. R.]: Moskovskoe obshchestvo ispytateley prirody, otd. zoologii, vol. 1, no. 26.
- \_\_\_\_\_, 1947, Irrigatsionnoe stroitel'stvo v basseynе Aral i voprosy rybnogo khozyatstva [IRRIGATION CONSTRUCTION IN THE ARAL BASIN AND QUESTIONS OF FISH MANAGEMENT]: Rybnoe khozyaystvo SSSR, no. 12.
- Rylov, V. M., 1933, Svedeniya o planktone ozera Balkhash. Issledovaniya ozer SSSR [EXISTENCE OF PLANKTON IN LAKE BALKHASH. RESEARCH ON LAKES OF THE U. S. S. R.]: Gidrometeoizdat, vol. 4.
- Samoylenko, V. S., 1947, Blizhayshee budushchee Azovskogo morya [IMMEDIATE FUTURE OF THE AZOV SEA]: GOIN, vol. 2, no. 15.
- Shnitnikov, A. V., 1936, Ozero Balkhash i solyanые озера его бассейна [LAKE BALKHASH AND SALINE LAKES OF ITS BASIN]: Vsesoyuznyy instituta gallurgii NIS NKTP, Solyanoy laboratorii, no. 2.
- \_\_\_\_\_, 1948, Vodnyy balans ozer Kulundinskogo i Kuchuk [HYDRAULIC EQUILIBRIUM OF LAKES KULUNDINSKY AND KUCHUK]: GGI, v. 4, pages 96-121.
- Solovyeva, N. F., 1950, K voprosu o dinamika solevogo balansa Aralskogo morya. Materialy po ikhtofaune i rezhimu vod basseyna Aralskogo morya [ON THE QUESTION OF DYNAMIC SALINE EQUILIBRIUM OF THE ARAL SEA. CONTRIBUTIONS ON ICHTHYOFAUNA AND REGIME OF THE WATERS OF THE ARAL SEA BASIN]: Moskovskogo ob-va ispytateley prirody, Moscow.
- Stepanova, K. M., 1948, Veshchestva, vybrasyvaemye vody Amu-Dar'i i Syr-Dar'i v Aralskoe more [SOLIDS AND SPRAY OF THE AMU-DARYA AND SYR-DARYA IN THE ARAL SEA]: DAN Uzb. SSR, no. 2.
- Suslov, S. P., 1947, Fizicheskaya geografiya SSSR [PHYSICAL GEOGRAPHY OF THE U. S. S. R.]: Moscow-Leningrad.



- Yunosov, G. R. , 1945, O prichine opresnenosti oz. Balkhash [ON THE CAUSE OF SHRINKAGE OF LAKE BALKHASH]: AN Kasakhskoy SSR, Seriya energeticheskaya, no. 2.
- Zaykov, B. D. , 1946, Sovremennyy i budushchy vodnyy balans Aralskogo morya [PRESENT AND FUTURE HYDRAULIC EQUILIBRIUM OF THE ARAL SEA]: Nauchno-issledovatel'skikh uchrezhdeny GUGMS SSSR, vol. 4, page 39.
- Zenkovich, V. P. , 1947, Donnye otlozheniya Aralskogo morya [DATA ON SILTING OF THE ARAL SEA]: Byulleten Moskovskogo ob-va ispytateley prirody, Novaya seriya, otd. geologii, vol. 22, no. 4.
- Zubov, N. N. , 1938, Morskie vody i l'dy [SEA WATERS AND SEA ICE]: Gidrometeorizdat, Moscow.

# NATURE OF NAPHTHENIC ACIDS IN BAKU CRUDE OILS AS A FUNCTION OF THE DEPTH OF OCCURRENCE<sup>1</sup>

by

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• translated by Royer and Roger, Inc. •

## ABSTRACT

The author analyzes data on the contents of naphthenic acid in crude oils. Characteristics and properties of naphthenic acids in oils of adjacent formations are compared. The final conclusion denies the existence of any general relationship between the content of naphthenic acids and the depth of occurrence of oils of the deposits of the Apsheron Peninsula. --Royer and Roger, Inc.

\* \* \*

In 1874 Eichler (ref. 1), and then Markovnikov, Ogloblin, Kharichkov and Zelinskiy, isolated some naphthenic acids from Baku crudes. These scientists also determined the chemical structure and properties of the naphthenic acids.

Pure naphthenic acids are saturated compounds, and are typical carboxylic acids in their chemical properties.

Although the content of naphthenic acids in petroleum is not large, significant variations are observed in different oils.

Naftali, who studied petroleum from different countries in relation to its naphthenic acid content, noted that the concentrations in the oils under study ranged from 0.07 to 2.4 percent. The largest amount of naphthenic acids was found in Rumanian petroleum. According to the data of F. E. Hickson (ref. 2, 1956), the content of naphthenic acids in some American crude oils is about 0.1 percent and in oils from the Middle East is even less than 0.01 percent. According to our data (ref. 3, 1954), the naphthenic acid content of high-quality petroleum from Azerbaidzhan ranges from 0.1 to 1.67 percent.

The content of naphthenic acids in petroleum of the eastern districts of the Soviet Union is insignificant.

The isolation of individual chemical compounds from the complex mixture of acids which is obtained from petroleum is an extremely difficult problem. The difficulty of isolating pure naphthenic acids grows as their boiling points and the complexity of their molecular structure increase. The acids are usually converted into their derivatives during the initial separation. The esters of naphthenic acids are mostly employed for this purpose.

There is a number of theories explaining the formation of naphthenic acids in petroleum. For example, V. M. Kharichkov (ref. 4, 1912) suggests that the oxidation of naphthenic hydrocarbons by photochemical processes, or by the Schaal process (the oxidation of naphthenic fractions by air at high temperatures in an alkaline medium), leads to the formation of monobasic naphthenic acids. Engler advocated the theory that naphthenic acids in petroleum are formed through the oxidation of naphthenic hydrocarbons.

G. S. Petrov (ref. 5, 1944) stated that acids obtained from the oxidation of paraffins are similar to fatty acids in their structure; acids with a cyclic structure, however, are principally obtained from the oxidation of kerosene and the higher petroleum fractions. L. P. Gurvich assumes that the concentrations of naphthenic acids in petroleum serve as proof of their organic origin, i. e., naphthenic acids are formed from the residues of fatty acids.

Despite the fact that naphthenic acids have been studied for more than 80 years, there are still many unexplained questions. Moreover, both the formation and structure of naphthenic acids have not been established with certainty.

N. I. Chernozhukov and S. E. Kreyn (ref. 6, 1936), who studied the effects of oxygen on naphthenic hydrocarbons, concluded, on the basis of their experimental data, that the oxidation of naphthenes takes place at the point of junction of the side chain, or at the point of contact of the rings in the case of polycyclic hydrocarbons. Having performed the comparative oxidation of naphthalene and a number of naphthenes with oxygen by heating at a pressure of 15 atmospheres, these same authors noted that naphthenic hydrocarbons are oxidized more easily than aromatic hydrocarbons. The sensitivity of the naphthenes toward oxidation grows with increasing molecular weight and presence of side chains, as is also the case with aromatic hydrocarbons.

In regard to the structure of naphthenic acids most research workers conclude, on the basis of experimental data, that the acids which occur in petroleum have five-membered naphthenic

<sup>1</sup>Translated from O. Prirode naftenovykh kislot v Bakinskikh neftyakh v zavisimosti ot glubiny zaleganiya; Uchenye Zapiski Azerbaidzhanskogo Gosudarstvennogo Universiteta imeni S.M. Kirova, no.2, p. 37-48, 1958. Technical content reviewed for IGR by Irving Breger.



rings. In this area of endeavor a large number of investigations have been conducted by N. D. Zelinskiy and his school. N. D. Zelinskiy transformed naphthenic acids into their constituent naphthenes through the conversion of the acids into methyl esters followed by the reduction of these compounds first to iodides and then to hydrocarbons by zinc dust. He showed that the low-molecular weight naphthenic acids in Caucasian petroleum consist largely of pentamethylene rather than hexamethylene derivatives.

Brun (ref. 7, 1898), and subsequently V. K. Kharichkov (ref. 8, 1909), have suggested that naphthenic acids in petroleum may belong to the hexahydrophenol series of acetic acid, which has six-membered naphthenic rings, and in which the carboxyl group is linked by means of the side chain rather than directly with the ring.

The structures and physicochemical properties of naphthenic acids have been studied but little in petroleum chemistry. Until now, not many of the individual monocyclic naphthenic acids, consisting mostly of derivatives of cyclopentane, have been isolated from various oils and studied. Kompa (ref. 9, 1929) isolated undecanaphthenic acid from Baku crudes by means of fractional distillation of methyl esters of naphthenic acids.

The naphthenic acids of middle petroleum fractions have been systematically studied, the naphthenic acids of the heavy oil fractions have received insufficient attention.

In this respect Alleman (ref. 10, 1929) has done interesting work on the study of the structure of high-molecular-weight acids isolated from the oily fractions of Texas crudes. Alleman discovered that high-molecular-weight acids cannot be represented by the formula  $C_nH_{2n-2}O_2$ , i. e., they do not belong to the series of monocyclic naphthenic acids. Their molecular weight varies from 250 to 376, they contain from 16 to 25 carbon atoms in a molecule and almost all belong to the  $C_nH_{2n-4}O_2$  and  $C_nH_{3n-6}O_2$  series. Their refractive indices are very high and vary from 1.4856 to 1.4965. Based on study of the acids which he isolated, Alleman suggested that bicyclic and tricyclic monobasic acids are present in the Texas crudes.

Braun (ref. 11, 1933) established that the greater part of low-molecular-weight naphthenic acids consists of monobasic acids, largely derived from cyclopentane, with the formula  $C_nH_{2n-2}O_2$ . In the naphthenic acid fractions (beginning, say, with  $C_{13}$ ) the bicyclic acids with the empirical formula  $C_nH_{2n-4}O_2$  are of principal importance together with, probably the  $C_nH_{2n-6}O_2$  polycyclic acids.

Muller and Pilate (ref. 12, 1936) reduced

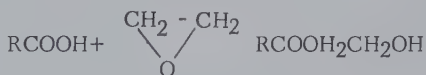
high-molecular-weight naphthenic acids, extracted from the tar distillate of low-paraffin petroleum, to naphthenic hydrocarbons (by Zelinskiy's method) in order to study their characteristics.

The molecular refraction of the hydrocarbons so synthesized showed that they contained admixed aromatic hydrocarbons. The authors explained this as resulting from the fact that naphthenic acids probably contain admixtures of aromatic carboxylic acids.

In order to ascertain the structure of high-molecular-weight naphthenic acids in Baku crudes, B. M. Rybak (ref. 13, 1948) performed a series of experiments by the Zelinskiy method, namely, the reduction of naphthenic acids to their constituent hydrocarbons. On analysis of the hydrocarbons obtained in this way, he concluded that the high-molecular-weight fractions of naphthenic acids of Balakhany heavy oil contain acids with aromatic or naphtho-aromatic structures.

Increased interest in oxygen-containing organic compounds is being shown in the Soviet Union and abroad at the present time. This is because of the greater use which is found for organic acids and their derivatives in the national economy. Research work on naphthenic acids has been expanded for some time; technical applications for such compounds are of the greatest economic importance in the soap manufacturing, textile, and varnish and paint industries.

Naphthenic acids will react readily with alcohols, with ethylene oxide, and with other similar compounds in the presence of catalysts to form complex esters. The latter compounds are exceptionally important and significant in the national economy. With regard to the reactions of organic acids with oxygen-bearing compounds, Ellis (ref. 14, 1936) notes that the reaction between ethylene oxide and organic acids serves as a very satisfactory method for the preparation of complex mono-esters corresponding to glycol. The author of the present paper, together with Prof. V. I. Isagulyants in the I. M. Gubkin Moscow Scientific Institute (MNI) succeeded in recovering the monoglycolic esters of naphthenic acids from catalytic reaction of naphthenic acids and ethylene oxide.



It should be noted that naphthenic acids are an important source of raw materials for the production of different chemical products.

Baku oils contain the largest quantity of naphthenic acids of all the oils in the Soviet Union, but these naphthenic acids have been insufficiently

studied. The present work was undertaken to study naphthenic acids in Azerbaidzhan crudes as a function of the depth of occurrence.

An aqueous solution of alkali was used for the extraction of naphthenic acids from crude oil or from its distillates. The substance called naphthenic acid was obtained through the decomposition of a solution of the salts of naphthenic acid in water, by leaching with an aqueous solution of caustic soda. The method termed "hot saponification" was employed for the determination of the potential content of naphthenic acids in oils and distillates (ref. 15, 1948). The potential content and certain properties of naphthenic acids in high-quality petroleum are given in Table 1. It is evident from the data in Table 1 that the high-quality oils from Azerbaidzhan contain from 0.1 to 1.67 percent of naphthenic acids. The oils having the poorest content of naphthenic acids are Kala U/D, Kala L/D, Kala of the Kala series, Kara-Chukhur U/D, Kara-Chukhur L/D, Surakhany selected, Surakhany ordinary, Surakhany heavy, Giurgya and Bukhta. The naphthenic acid content of these oils ranges from 0.1 to 0.35 percent. The oils rich in naphthenic acids are Balakhany oily, Balakhany heavy, Romany, Binagada, Lokbata oily, Puta oily, Neftyanyye Kamni, Artematarry, Neftechaly, Bibi-Eybat and Kergez. The naphthenic acid content of these oils ranges from 0.83 to 1.67 percent. The oils Bibi-Eybat paraffinic, Yasama, Umbaku and Busovny occupy an intermediate position with respect to their acid content. The

naphthenic acid content of these oils ranges from 0.4 to 0.63 percent. In addition to the potential content, the acid numbers and molecular weight of the naphthenic acids are given in Table 1.

From the data of Table 1, it is possible to conclude that the content of naphthenic acids is low in paraffinic oils.

If the concentrations of naphthenic acids in the Kala petroleum deposit are analyzed (table 2), it appears that the naphthenic acid content of oil decreases with depth while the paraffin content increases.

Table 2

Name of oil	Content of oil in percent	
	Naphthenic acids	Paraffin
Kala of the upper division	0.19	1.59
Kala of the lower division	0.14	2.71
Kala of the Kala formation	0.11	4.00

There is a similar picture for the Surakhany deposit (table 3).

Table 3

Number	Name of oil	Content of oil in percent	
		Naphthenic acids	Paraffin
1	Surakhany selected	0.19	4.62
2	Surakhany ordinary	0.17	3.20
3	Surakhany heavy	0.15	2.5

Table 1. Potential content and properties of naphthenic acids in selected oils

Name of oil	Content in percent		Naphthenic acids and their properties		
	Tars	Paraffins	Yield in percent of oil weight	Acid number mg. KOH/g	Molecular weight
Kala U/D	17	1.59	0.19	150	335
Kala L/D	20	2.71	0.14	150	350
Kala Formation	-	4.0	0.11	160	350
Surakhany selected	8	4.62	0.19	158	335
Surakhany ordinary	10	3.20	0.17	178	315
Surakhany oily	24	0.91	0.43	182	308
Surakhany heavy	21	2.5	0.15	180	311.6
Kara-Chukhur U/D	8	6.0	0.11	146	384
Kara-Chukhur L/D	18	4.95	0.25	151	370
Romany II high quality	16	0.70	1.20	188	300
Balakhany heavy [ordinary?]	14	1.42	0.97	181	310
Balakhany heavy	29	0.62	1.67	195	288
Binagady	30	0.63	0.83	200	280
Bibi-Eybat light	20	0.76	0.83	195	288
Bibi-Eybat paraffinic	25	2.09	0.5	160	350
Bukhta	24	1.98	0.35	164	342
Lokbata oily	25	0.91	1.0	185	303
Puta oily	30	0.80	0.96	190	295
Yasama	30	2.40	0.40	180	311.6
Neftyanyye Kamni	24	1.0	1.22	174	322
Umbaku	44	1.2	0.54	196	287
Buzoyny	30	0.99	0.45	195	288
Arten	44	0.3	1.35	220.7	254
Neftechaly	50	0.51	1.19	220	225
Giurgya	22	1.7	0.26	160	346
Kergez	38	0.25	0.83	200	280



The tendency for the naphthenic acid content of the Surakhany deposit to decrease with the depth of occurrence persists, but then the paraffine content of the oil also decreases with the depth.

The oils of the Kara-Chukhur deposit possess unique properties in relation to naphthenic acids. (table 4).

Table 4

Name of oil	Content in percent of oil	
	Naphthenic acids	Paraffin
Kara-Chukhur U/D	0.11	6.0
Kara-Chukhur L/D	0.25	4.95

Although the oils of the Kara-Chukhur deposit conform to the general rule for naphthenic acids, i. e., a decrease in the content of naphthenic acids with increasing paraffin content, the content of naphthenic acids increases, however, with the depth of occurrence. The relationship between the naphthenic acid and paraffin content of oils of the Balakhano-Sabunchi deposit is as seen in Table 5.

Table 5

Name of oil	Content in percent of oil	
	Naphthenic acids	Paraffin
Romashka p. t.	0.97	1.42
Balakhany oily	1.20	0.70
Balakhany heavy	1.67	0.62

This relationship in the Bibi-Eybat deposit is seen in Table 6.

Table 6

Name of oil	Content in percent of oil	
	Naphthenic acids	Paraffin
Bibi-Eybat light	0.83	0.76
Bibi-Eybat paraffinic	0.50	2.09

All the five above-mentioned deposits of the Apsheron Peninsula possess a certain regularity when the paraffin content is high, the naphthenic acid content is low.

Although it should be noted that the first three petroleum deposits are approximately of a single type with regard to their quantitative content of naphthenic acids, it is impossible to say the same with regard to the properties of these naphthenic acids. Thus, for example, the acid numbers of naphthenic acids in the Kala oils range from 150 to 160; for naphthenic acids of the Surakhany petroleum deposit they range from 158 to 180; and for the oils of the Kara-Chukhur deposit from 146 to 151. The qualita-

tive difference of naphthenic acids isolated from petroleum of the Kala, Surakhany and Kara-Chukhur deposits is more markedly illustrated by their molecular weight ranges, which are from 335 to 350, 312 to 335 and 370 to 384 respectively.

It is evident from these qualitative proofs that the naphthenic acids in the petroleum of the three above-mentioned deposits differ one from the other. Especially distinctive is the petroleum of the Kara-Chukhur deposit, whose naphthenic acids differ from those of the other oils of Azerbaidzhan in their very low acid number and in their very high molecular weight.

Naphthenic acids isolated from petroleum of the Balakhano-Sabunchi deposit have the following properties: the acid numbers range from 181 to 195, and their molecular weights range from 288 to 310. For the naphthenic acids of the Bibi-Eybat deposit, the acid numbers vary from 160 to 195, while the molecular weights range from 288 to 350.

Naphthenic acids of petroleum from marine deposits are characterized by the following properties, (see table 7).

Table 7

Name of oil	Properties of Naphthenic acids	
	Acid number	Molecular weight
Bukhta Il'ich	164	342
Artem paraffinic	160	346
Artem tarry	220	254
Neftyanyye Kamni	174	322

Having considered all the data relating to the content and properties of naphthenic acids in various oils from Azerbaidzhan, it may be stated that tarry and low-paraffin oils contain the largest quantity of naphthenic acids. The naphthenic acid content of the oils decreases with increasing paraffin content.

Naphthenic acids of paraffinic oils possess the lowest acid number and the highest molecular weight. The naphthenic acids in petroleum of the Kara-Chukhur deposit are particularly noteworthy in this respect. The high molecular weights of these naphthenic acids may, in all probability, well be explained by the polycyclic structure of the acids and by the iso-structure of the side chains. The properties and content of naphthenic acids in petroleum of the upper and lower divisions of any particular deposit are not markedly different. However, there are marked variations in the chemical composition and hydrocarbon structure of the soil in the upper and lower division of each deposit in the Apsheron Series that has both upper and a lower division.

It follows from the data presented above that the petroleum of each deposit contains naphthenic acids which possess different properties from those of the other deposits.

Naphthenic acids occur in the organic fraction of natural petroleum. As has already been mentioned above, there are a number of theories explaining the formation of naphthenic acids from petroleum (ref. 16, 1926). In Von Braun's opinion (ref. 17, 1931), naphthenic acids are formed as a result of the oxidation of readily oxidizable cycloparaffins, either through alkaline flushing or by the distillation of petroleum. In this respect Puhala (ref. 18, 1933) states that the distillates of Baku petroleum contain a 12-fold higher concentration of naphthenic acids than the crude oil. Our data do not corroborate the contentions of these authors because all the naphthenic acids were separated from petroleum without any distillation; both the yield and the naphthenic acid content of crude oil and their total content in the distillates correspond to each other. Secondly, under such conditions as the distillation of petroleum (e.g., at a temperature of 340°C) and leaching for a short time and at low temperatures, naphthenic hydrocarbons cannot easily be oxidized to naphthenic acids.

The suggestions of L. G. Gurvich, that the concentrations of naphthenic acids in petroleum serve as proof of their organic origin and that naphthenic acids were formed from the residues of fatty acids, is not corroborated by our data. The content of naphthenic acids in petroleum as a function of the depth of occurrence is shown in Table 8. It is evident from the data

there is no clear-cut regularity in the relation between the acid contents and the depth of occurrence. If it is assumed that naphthenic acids are formed from the residues of fatty acids, as L. G. Gurvich suggests, the acid content of the lower formations at Apsheron, especially in the Diatomov and Kala formations or in the Maykop formation, ought to be much larger than in the overlying formations. This, however, is not the case. Petroleum occurring in more ancient strata, such as those of Devonian age, has an almost negligible content of naphthenic acids.

It should be noted that there is no definite regularity in the distribution of naphthenic acids for the whole productive rock sequence. Each individual oil (the oil of each formation) at Apsheron contains a certain quantity of naphthenic acids. It is apparent from Table 8 that all the individual oils contain different quantities of naphthenic acids.

The similarly named formations of various deposits on the Apsheron Peninsula contain oils with dissimilar concentrations of naphthenic acids, despite the fact that the beds were laid down in approximately the same geological period. As shown below, the naphthenic acid contents of petroleum of the Sabunchi formation are:

	Percent
In the Kala deposit	0.16
In the Surakhany deposit	0.11
In the Balakhany deposit	0.9
In the Bibi-Eybat deposit	0.8

TABLE 8. Content of naphthenic acids as a function of the depth of occurrence of oils of the Apsheron peninsula, in weight percent

Name of formations	Kala deposit	Surakhany deposit	Balakhany deposit	Bibi-Eybat deposit	Karadag deposit	Binagady	Buzovny	Siazan deposit
Surakhany	0.11	0.12	1.22	0.87				
Sabunchi	0.16	0.11	0.90	0.80				
Balakhany	0.21	0.10	1.14	0.79	1.06			
NKG	0.24	0.16		0.47				
NKP	0.18	0.24	1.55	0.63				
Kirmaku	0.22	0.43	1.67	0.42	0.5	1.34	0.51	
Podkirmaku	0.26	0.43	1.25	0.56	0.39	1.25	0.57	
Kala	0.15	0.19				1.62		
Diatomov								
Maykop								0.28

of Table 8 that the very lowest formations at Apsheron, namely Kala and Diatomov, contain less naphthenic acid than the formations which overlie them, such as PK and KS. The naphthenic acid content of oil of the Maykop formation is similarly 0.28 percent. The oil occurring at depth in such petroleum deposits of western Apsheron as Binagady, Bibi-Eybat and in the oil of the Karadag area clearly has a reduced content of naphthenic acids. For such petroleum deposits as Kala, Surakhany and Balakhany,

The content of acids in oils of the Podkirmaku formation:

	Percent
In the Kala deposit	0.26
In the Surakhany deposit	0.43
In the Balakhany deposit	0.56

All data cited above indicate that it was not the residues of fats or fatty acids which were responsible for the formation of the naphthenic



acids in the productive series at Apsheron, but the oxidation of readily oxidizable hydrocarbons, principally those with bicyclic and polycyclic structures.

Primary oil or petroliferous matter originates in a certain formation, and lies for millions of years in this environment with various host rocks under different temperatures and pressures. The oil is subjected to various natural catalytic processes and changes its original composition, during which some of the cyclic hydrocarbons are, in all probability, oxidized to naphthenic acids.

On the basis of the data about naphthenic acids in individual oils of the Baku district it is possible to state that their content varies widely in relation to the depth of occurrence in each deposit and also between the deposits.

Thus, for example, the naphthenic acid content from the Surakhany to Podkirmaku formations of the Kala deposit varies from 0.11 to 0.26 percent, and in the Surakhany deposit from 0.1 to 0.43 percent, while the naphthenic acid content of the Balakhano-Sabunchi deposit lies in the range 0.9 to 1.67 percent. In the Bibi-Eybat deposit, a different pattern is observed, that is, the naphthenic acid content of the formations varies from 0.83 to 0.42 percent.

As a result of the detailed examination of much accumulated material, it is possible to suggest that the naphthenic acids, and for that matter oil as a whole in the Baku petroleum, are secondary products; the former must originate through the oxidation of cyclic hydrocarbon groups during the deposition of oil in the formations.

The results of the detailed analysis of some narrow fractions of pure naphthenic acids iso-

lated from the kerosene-gasoline fractions are given in Table 9. Their elementary composition and molecular weights were determined, on the basis of which the series and the empirical formulas were then calculated.

## CONCLUSIONS

1. Paraffinic oils and their heavy oil fractions contain the least quantity of naphthenic acids. Low-paraffinic and tarry oils contain the greatest quantity of naphthenic acids. Paraffinic oils contain acids with a relatively high molecular weight.

2. Every petroleum deposit on the Apsheron Peninsula is characterized by naphthenic acids that are peculiar only to a given deposit. Naphthenic acids in oils of adjacent formations of the same deposit differ markedly from each other in their characteristics and properties.

3. As a result of the detailed examination of much factual material about naphthenic acids, it is possible to suggest that naphthenic acids (and, for that matter, oil as a whole) which occur in Baku petroleum are secondary products; the former must originate through the oxidation of certain groups of cyclic hydrocarbons during the deposition of oil in the formations.

4. Naphthenic acids of the kerosene-gasoline fractions of Baku petroleum have mainly bicyclic and polycyclic structures.

5. It is impossible to deduce any general relationship between the content of naphthenic acids and the depth of occurrence of oils of the deposits of the Apsheron Peninsula. Each deposit has its own inherent characteristics.

TABLE 9. Naphthenic acids isolated from the kerosene-gasoline fractions of Baku high-quality oils

Range of boiling points in °C	Specific gravity	Molecular weight	Index of refraction 20/D	Elementary composition			Series	Empirical formulae
				C	H	O		
296-297	0.9693	294.8	1.4626	76.90	11.76	11.18	$C_{19}H_{34.7}O_{2.07}$	$C_nH_{2n-3.3}O_{2.07}$
303-304	0.9771	303	1.4649	77.71	11.64	10.65	$C_{19}H_{35.2}O_{2.07}$	$C_nH_{2n-4}O_{2.02}$
306-308	0.9800	360	1.4687	76.54	11.25	12.21	$C_{23}H_{40.5}O_{2.7}$	$C_nH_{2n-5.5}O_{2.7}$
311-312	0.9830	375	1.4712	78.68	11.19	10.13	$C_{24}H_{42}O_{2.4}$	$C_nH_{2n-6}O_{2.4}$
314-135	0.9820	380	1.4734	74.27	10.81	14.92	$C_{24.5}H_{45}O_{2.5}$	$C_nH_{2n-4}O_{2.5}$
315-316	0.9838	373	1.4740	74.75	11.01	14.24	$C_{23.5}H_{41.5}O_{3.3}$	$C_nH_{2n-5.5}O_{3.3}$
316-318	0.9853	393	1.4747	74.05	10.88	15.07	$C_{24.2}H_{42.8}O_{3.7}$	$C_nH_{2n-5.6}O_{3.7}$
327-330	0.9882	408	1.4791	78.10	11.50	10.10	$C_{26.5}H_{47}O_{2.6}$	$C_nH_{2n-6}O_{2.6}$
330-334	0.9906	436	1.4807	79.24	11.60	9.16	$C_{28.7}H_{50.6}O_{2.5}$	$C_nH_{2n-6.8}O_{2.5}$

## REFERENCES

1. [Eichler, ] Bull Soc. Natur., Moscow, 45, 1874.
2. Hickson F. E., Report of IV International Petroleum Congress, vol. V, 1956, 240 p.
3. [Ashumov, G. G., ] AzNIN NP, Scientific-technical report for 1954.
4. [Karichkov, V. M., ] Neftyanoye Delo, 10, 14 (1912).
5. [Petrov, G. S., ] Sinteticheskiye Zhirnyye kisloty, [SYNTHETIC FATTY ACIDS]: 1944, p. 7.
6. Chernozhukov, N. I., Kreyn, S. E., Okislaiyemost mine alnykh masel [OXIDATION OF MINERAL OILS], ONTI, p. 155, 1936.
7. [Brun, ] Chemie Ztg., 900, 1898.
8. [Kharichkov, V. K., ] Zh. R. F. Kh. O. Journal of the Russian Physiochemical Society] 1150, 1909.
9. [Kompa, ] Berichte (62), 1562, 1929.
10. [Alleman, ] Chem. Abs. (23), 696, 1929.
11. [Braun, ] Berichte (66), 1949, 1933.
12. [Muller and Pilat, ] Brennstoff Chemie (24), 1936.
13. Rybak, B. M., Naftenovyye kisloty [NAPHTHENIC ACIDS]: Gostoptekhizdat, 1948, p. 19. In Russian.
14. Ellis, K., Khimiya uglevodorodov nefi [CHEMISTRY OF PETROLEUM HYDROCARBONS]: v. 1, 1936, p. 586. In Russian.
15. Rybak, B. M., Analiz nefi i nefteproduktov [ANALYSIS OF OILS AND PETROLEUM PRODUCTS]: Aznefteizdat, 1948, p. 427. In Russian.
16. Tiutinnikov, Neftanoye Khozyaystvo [OIL ECONOMY]: 10, 797, 1926.
17. [Von Braun, ] Ann. 490, 100, 1931.
18. [Puhala] Chemie Ztg: 57, 273, 294, 1933.



# CERTAIN RELATIONSHIPS IN THE COMPOSITION OF CRUDE OIL<sup>1</sup>

by

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• translated by Royer and Roger, Inc. •

## ABSTRACT

Certain relationships in the composition of petroleum are reviewed as functions of their degree of transformation. The authors base their discussion on a thermodynamic analysis of the probability of a given reaction and on the actual analyses of petroleum. Reviewed data were limited to hexane isomers; data for other hydrocarbons confirmed the authors' conclusions. --Royer and Roger, Inc.

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Petroleum in its underground reservoir is a thermodynamically closed system, and the changes in it may be considered, in a most general way, as energy changes. It has been shown experimentally that even such chemically inert substances as hydrocarbons can be transformed at relatively low temperatures, especially in the presence of natural catalysts of the aluminosilicate type, into hydrocarbons possessing less free energy than the parent hydrocarbons. In the course of these transformations petroleum becomes enriched in low-molecular-weight hydrocarbons, particularly those of the methane series. This causes a decrease in the specific gravity of petroleum and its methanization. Thus, the type of petroleum is determined, not by its absolute geologic age, but by the degree of its transformation. Only a statistical approach to the problem of the origin of petroleum justifies the statement that the geologically older petroleum is also the most strongly metamorphosed. One of the proofs of this statement is the fact that the average specific gravity of the world's petroleum decreases continuously with increasing exploitation of petroleum from the deeper horizons, i. e. of petroleum of statistically greater geologic age.

The transformation hypothesis satisfactorily explains the formation of the different types of petroleum by late postburial transformation of hydrocarbon molecules rather than by differences in the character of the mother-substance. It also answers the question as to why a great difference exists between the extreme types of petroleum while modern oozes and sapropel are of relatively uniform composition.

From the point of view of the transformation hypothesis, the sum total of the chemical and

physical properties of each oil type is only a transitional stage in the process of evolution of the petroleum-forming material. A change in a single property of petroleum inevitably brings about a change in all other properties. Therefore, it is possible to judge the degree of transformation by any property of petroleum which is the most amenable to study. All other properties may be regarded, then, as transformations within the system, for evidently all properties are mutually dependent. From this arises the concept of patterns in the composition of petroleum. All theoretically possible patterns are only different interrelated phases of a single process. These regularities are significant, for not only do they confirm the correctness of the hypothesis of the transformation of petroleum in nature, but they also throw considerable light on the inner processes to which petroleum is subjected during its evolution.

Although all petroleum undergoes continuous transformation, the intensity of change is not the same for all compounds entering into its composition but depends on the characteristic properties of each type of compound. It is clear that the transformation of the naphthenes may be rather profound, while that of the hydrocarbons of the aliphatic or aromatic series will not be very noticeable. This, of course, will not be reflected in the total content of the last two series of hydrocarbons in petroleum as a whole, but will definitely affect the composition of its individual fractions. For example, the content of the simplest naphthenes in the benzene fraction of the Grozny paraffin-base petroleum is much lower than in the benzene of the Baku naphthene-base petroleum; considering the petroleum as a whole, however, the naphthene content is approximately the same in both cases, suggesting that the simplest naphthenes form before the mass of the light aliphatic hydrocarbons.

The formation of hydrocarbons of low boiling point and low molecular weight during the process of petroleum transformation consists, in the final analysis, in the migration of a part of the hydrogen from one molecule into another. As one molecule gains hydrogen, another be-

<sup>1</sup>. Translated from *Nekotorye zakonomernosti v sostave neftey*; Trudy Vsesoyuznogo neftyanogo nauchno-issledovatel'skogo geologorazveddochnogo instituta, v. 123, Geokhimicheskii sbornik, no. 5, Leningrad, 1958. Reviewed for technical content by Irving A. Bregier.

comes impoverished in it to the same degree and becomes enriched in carbon, thus forming a complex compound of high molecular weight. In this way are formed the secondary resinous substances that are typical of transformed petroleum but not at all characteristic of un-metamorphosed petroleum.

It was observed long ago that the petroleum from the deeper horizons, i. e. those that are geologically older, have lower specific gravity. This was one of the first regularities in the composition of petroleum to be noted. Many others have been discovered since, and some of them will be partially reviewed in this paper. Investigation of these regularities and their causes is one of the most interesting phases of the geochemistry of petroleum. It discloses the sequence of transformations, their mechanisms, relative stabilities of the hydrocarbons of the different series and, moreover, shows clearly that the transformations occur in strict adherence to the laws of thermodynamics. It may also be said that thermodynamics is the key to the explanation of some of the regularities deduced directly from empirical observations. Some of the regular variations in the composition of petroleum relate to constituents other than the hydrocarbons and to optically active compounds.

Much less known are the transformations of petroleum effected by external factors. It may be supposed, of course, that the oxidation of petroleum at the surface must spread to its entire mass and especially to those constituents which are the most susceptible to the action of atmospheric oxygen. The same is true of the sulfurization of petroleum, but at present the data are too few to enable us to speak of the selectivity of these reactions and, although there are many hypotheses, it is not at all clear what particular petroleum types will form under the influence of external factors. The role of some of the components of the enclosing rocks, especially sulfates and carbonates, in determining the type of petroleum is also unknown, for the existing hypotheses and opinions are still far from providing a unique solution of this problem and have not been confirmed experimentally.

The various transformations of petroleum at great depth by bacteria must be considered as being caused by external factors; in spite of the many ideas on the subject, however, the role of bacteria is no better understood than the effects of the specific components of the enclosing rocks, such as the carbonates and sulfates.

#### THE CONTENT OF HETEROELEMENTS AND THE OPTICAL ACTIVITY OF PETROLEUM

A living organism is characterized by a more or less prolonged preservation of the general plan of structure of its molecules as a result of

exchange with the surrounding medium, while an inorganic substance is characterized by spontaneous breakdown of its components. The organism receives the energy necessary for maintaining the stability of its molecules from an outside source, from the sun if it is an autotrophic organism, and from the substance of other organisms if it is heterotrophic. When it is no longer possible to assimilate energy from external sources, the basic factor of stability is lost and the internal energy of the molecules becomes the source of further activity.

Every organic molecule has a greater amount of free energy than the initial substances of photosynthesis, carbon dioxide and water; inasmuch as all matter in nature spontaneously strives toward minimum free energy, transformations will tend toward a decrease in the energy of the system within the limits between  $\text{CO}_2$  and  $\text{H}_2\text{O}$  (Andreyev, 1957).

The decrease in free energy may occur in different ways depending on external conditions. In the presence of an excess of oxygen it follows the shortest route and carbon dioxide and water are formed once again. The entire supply of free energy is converted into thermal energy and is lost in space without a trace.

The decrease in free energy becomes more complicated when oxygen is deficient or absent. It must be attained, then, through the possibilities provided by the organic system itself. The lowering of the free energy level, in this case, is achieved by a reconstruction of molecular bonds that previously existed in the living organism. During this reconstruction, low-energy bonds are exchanged for higher-energy bonds by redistribution (reapportioning) of elements within the system. This occurs in such a manner that the heterogeneous elements (oxygen, hydrogen, sulfur and nitrogen) accumulate preferentially in some parts of the system around one or more selected carbon atoms. The parts of the system overloaded with heteroelements become unstable and tend to break down spontaneously with the separation of the simplest molecules containing an atom (or atoms) of carbon and fully saturated with oxygen, hydrogen or other elements.

Thus, the external processes of spontaneous transformation of organic substances in a non-oxidizing environment consist of the separation from the organic matter of heteroatoms in the form of the simplest compounds, partly inorganic, and formation of a certain amount of mobile products with high free energy in the form of hydrocarbons. The main part of the organic matter becomes more and more enriched in carbon, tending towards graphite as a limit.

The accumulation of hydrogen-enriched mobile products leads to formation of petroleum deposits. The initial petroleum contains a



certain amount of heteroelements held in the complex molecules of resinous non-hydrocarbon compounds. As the supply of reactive compounds diminishes, so, naturally, does the rate of transformation of the remaining mass, and further evolution of petroleum in the deposit proceeds at a slower tempo. To this slowing down of the process of transformation we owe the presence of oil in the earth's crust.

Although the rate of transformation slows down considerably, the general trend of the process remains unchanged, and the heteroelements continue to separate in the form of the simplest compounds. If the petroleum system were completely isolated, it would, in the course of time, accumulate these simplest compounds containing the main mass of heteroelements, while the main part of the oil would be gradually carbonized. Actually, the most mobile products of transformation, the lightest hydrocarbons and inorganic compounds, escape to an extent depending on the degree of isolation. The substances with the slowly rising carbon content and decreasing solubility pass into the solid phase, and petroleum becomes more and more "reduced", while the last heteroelement, hydrogen, escapes at an even slower rate, largely in the form of methane, which forms with other light hydrocarbons.

The composition of petroleum in the advanced stages of transformation becomes increasingly simple because the simpler the structure of a compound in the homologous series, the less its supply of free energy. Connected with this process is the well-known decrease in the optical activity of crude oils with increasing alteration. It can be shown also that asymmetric organic molecules have higher free energy than do symmetrical ones of the same composition; hence, the change of the former into the latter is quite normal. For this reason, with intensification of transformation within the petroleum system, the number of compounds containing heteroelements of asymmetric molecules gradually decreases, and the system tends spontaneously towards thermodynamic equilibrium.

As has already been mentioned, the general trend of evolution of petroleum consists in successive changes in its composition resulting from non-reversible processes accompanied by separation of carbon dioxide, water, hydrogen sulfide, ammonia and methane. From this

point of view, the non-hydrocarbon constituents of petroleum (except, perhaps, for sulfur compounds in highly sulfurized oils) must be regarded as relict compounds, representing incompletely transformed mother-substance or, at least, the products of the early stages of its transformation into petroleum hydrocarbons.

The oxygenated substances of petroleum include different types of oxygen compounds which can be placed, according to their content of functional groups, into three classes:

1. Those compounds containing hydroxyl groups and forming high molecular weight alcohols and phenols.
2. Organic acids, i.e., fatty and naphthenic acids of different molecular weights.
3. Compounds containing oxygen in linked groups and other neutral oxygen compounds.

The principal reactions of these compounds during geologic time are decarboxylation and dehydration resulting in the formation of various hydrocarbons. Therefore, decrease in the content of oxygenated compounds in petroleum is also an index of the degree of its transformation and is manifested in the lowering of the tar content, of the acid value, and of saponification number or in decrease in the content of naphthenic acids.

Rather extensive analytical data are now available on the characteristics of petroleum from different deposits. The most interesting in this respect are the multizone deposits of Northern Caucasus and Emba, where the decrease in the content of non-hydrocarbon compounds in petroleum can be related quite clearly to increasing depth of the oil-bearing sandstones (table 1).

Table 1 shows clearly that the petroleum lying beneath the overthrust limb of the Old Grozny anticline are more strongly altered than those from the overthrust limb. In general, the oils from beneath the thrust contain less asphalt and tar components and are less acidic, indicating that the decrease in the content of non-hydrocarbon compounds is a function of the degree of their metamorphism. Evidently the geochemical conditions beneath the Old Grozny thrust were more favorable to the

TABLE 1. Acidity and asphalt-tar content in the petroleum of the Old Grozny region according to the average data of A.I. Bogomolov and N.V. Strigaleva (1953)

Old Grozny anticline	Tar and asphalt content in petroleum, percent		Acidity, mg KOH per g of oil	
	In the overthrust	Beneath the overthrust	In the overthrust	Beneath the overthrust
Karaganskian sandstones, beds I to IX	10.2	6.2	2.09	0.16
Chokrakian sandstones, beds X to XVI	8.2	5.0	0.57	0.13



transformation of petroleum than those in the over thrust limb. These favorable conditions may have been determined by the greater depth of the oil beneath the thrust and the higher temperatures prevailing there.

Formation of the thrust with the throw of 1,000 meters placed part of the petroleum reservoir beneath the overturned limb of the Old Grozny anticline in a relatively high temperature environment for a long period of time. According to measurements in the wells, the temperature of bed I averages 20°C in the overthrust limb and 56°C beneath it, the difference being 36°. The temperatures of bed XVI in the overthrust and underthrust blocks are 51° and 78°C, respectively. Here, also, the temperature of the bed in the underthrust block increases by 27°, and this must have inevitably affected the metamorphism of petroleum and diminution of its content of heteroelements.

Another, no less interesting example illustrating the decrease in heterogeneous compounds in petroleum is to be found in the reservoirs in the Cretaceous and Jurassic deposits of Kulsara on the southern Emba River (table 2).

content) changes with their density and the asphalt content. Both acidity and ether content diminish from the oils of the Albian horizon to those of the Middle Jurassic sands and clays. This is especially clearly shown by the decrease in the ether content, which is 4 times lower in the Jurassic as compared with the Cretaceous oils. As the depth at which petroleum undergoes transformation increases, the amount of sulfur and nitrogen compounds in it diminishes. These regularities, as well as the decrease in specific gravity with depth, can be regarded as a law only after the phenomenon has been analyzed statistically on the basis of numerous data on the characteristics of petroleum. These characteristics will be discussed a little later.

It has already been mentioned that optical activity decreases with the depth of transformation of petroleum. This follows from the premise that the process of alteration of organic matter ultimately producing methane and graphite involves simplification of the structure of organic molecules and diminution of their asymmetry. Before demonstrating this point, however, it is necessary to review certain data on the optical activity of petroleum. The available data on

TABLE 2. General characteristics of petroleum from Kulsara, Southern Emba, according to A.I. Bogomolov and F.B. Indenbom (1951)

Geological age of reservoir rocks	Specific gravity of oil	Paraffin content, percent	Tars extracted with H <sub>2</sub> SO <sub>4</sub> , percent	Sulfur content, percent	Nitrogen content, percent	Acidity, mg KOH per g of oil	Ether content mg KOH per g of oil	Fractions distilled below 550°C, percent	Residue, boiling point over 550°C, percent
Cretaceous, lower Albian	0.889	2.1	9.0	0.36	0.07	0.20	0.67	82	18
Cretaceous, lower Aptian	0.882	4.0	6.0	0.35	0.07	0.20	0.34	80	20
Cretaceous, upper Neocomian	0.879	3.3	5.5	0.27	0.07	0.20	0.33	85	15
Upper Jurassic	0.862	6.4	2.3	0.12	0.06	0.07	0.21	88	12
Middle Jurassic, upper coal-free formation	0.823	7.3	1.8	0.09	0.05	0.05	0.08	92	8
Middle Jurassic, lower coal-free formation	0.793	-	1.5	0.09	0.03	0.05	0.15	-	-
Middle Jurassic, sand and clay formation	0.793	4.1	1.5	0.09	0.03	0.05	-	91	9

The data of Table 2 show regular changes in the composition of petroleum with increasing geochemical transformation. The specific gravity and the content of asphalt diminishes from the oils of the lower Albian horizon to the oils of the Middle Jurassic arenaceous-argillaceous rocks. In the Cretaceous oils the maximum content of asphalt, as determined by the sulfuric acid method, is 9 percent, while in the Jurassic oils it is only 1.5 percent.

The acidity of the oils (free acid and ether

the optical activity of petroleum indicate that all petroleum is dextrorotatory.<sup>2</sup>

Strong optical activity is characteristic of the heavy petroleum fractions, while the light ben-

<sup>2</sup>

The few references in the literature to levorotatory petroleum are not convincing from either theoretical or experimental point of view. Taking petroleum as a whole, the right-handed rotation is more probable.

zene and ligroin fractions are almost inactive. According to a number of recent investigations, the petroleum hydrocarbons that rotate the plane of polarization of light are naphthenes and aromatic hydrocarbons or their mixtures, while the members of the methane series are optically inactive. Thus, optical activity is essentially the property of polycyclic hydrocarbons and the lubricant fractions of the naphthene-base oils show strong rotary polarization. On the other hand, the highly transformed oils composed almost entirely of paraffins, such as the oils of the Minusinsk basin, are optically inactive.

These data on optical activity have been confirmed by Oakwood (1952), who separated hydrocarbons with a rotation of  $+39^\circ$  and melting point of  $160^\circ\text{C}$  from the lubricant fractions of petroleum. A detailed investigation of isolated optically active compounds showed that they are products of transformation of cholesterol or similar substances whose biogenic nature is beyond doubt. There is reason to suppose, therefore, that optical activity of petroleum is, in a sense, of a relict nature and is inherited from the organic remains that are the source of hydrocarbons in the earth's crust.

The transformation of oil by the breakdown of molecules decreases optical activity. If the initial molecules were characterized by a definite angle of rotary polarization, the angle in the newly formed molecules will, in general, be much smaller. The optical activity of the fractions of intermediate boiling temperature is inherited directly from the parent organic matter through the heavier hydrocarbons from which they were formed. This follows from theoretical considerations and is confirmed by experimental data on the low-temperature transformation of the heavy petroleum fractions. It was shown in one of the investigations (A. I. Bogomolov and I. V. Shklyar, 1950) that when heated at  $250^\circ\text{C}$  for six hours with unactivated clay, the lubricant fraction produces light distillates absent in the raw material. The new fractions of low and intermediate boiling temperature are mixtures of aliphatic, naphthenic and aromatic hydrocarbons completely free of unsaturated hydrocarbons. It is noteworthy that the hydrocarbons produced by thermocatalysis were noticeably active and dextrorotatory like the initial fractions from which they were formed (table 3).

It follows from Table 3 that the lubricant fractions, after being heated with clay, became considerably less active, and the newly formed fractions were only slightly active. On the whole, the optical activity of the system diminished. This was caused by destruction of a fraction of the molecules having asymmetric carbon atoms. Outwardly this was manifested by decrease in the amount of polycyclic hydrocarbons and the formation of the simplest hydrocarbons of the aliphatic, naphthenic and aromatic series, whose optical activity is very slight or nil. Therefore, the transformation of hydrocarbons consisting in the destruction of polycyclic structures and resulting in the formation of a mass of paraffins lowers the optical activity of petroleum.

Inasmuch as the transformation of petroleum is connected with progressive paraffinization, the statistically older oils have a much smaller rotatory power than the younger oils. According to G. A. Amosov's data (1952), the rotatory power of the Cenozoic petroleum averages  $+1.00$ , in the Mesozoic petroleum it diminishes to  $+0.35$ , and in the Paleozoic petroleum, to  $+0.26$ .

The observed decrease in the rotatory power of petroleum with age is in harmony with other changes, especially in specific gravity and the degree of paraffinization, and must be regarded as a well-established relationship.

#### DECREASE IN SPECIFIC GRAVITY OF PETROLEUM WITH DEPTH AND GEOLOGICAL AGE OF ENCLOSING ROCKS

One of the important relationships quite firmly established for all petroleum is decrease in specific gravity with increase in the degree of transformation. This empirically deduced fact has a theoretical basis.

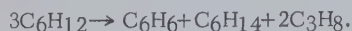
To show this, let us review certain thermodynamically possible processes. The process of redistribution of the elements in a system composed entirely of naphthene hydrocarbons must sooner or later create a new system consisting of naphthenes, aromatic hydrocarbons

TABLE 3. Optical activity  $[\alpha]_D$  of crude oil and the products of thermocatalysis after A. I. Bogomolov and I. V. Shklyar (1950)

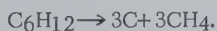
Temperature range of formation of fractions, $^\circ\text{C}$	Crude oil		Catalysate	
	Raw fractions	Sulfurized fractions after removal of aromatic hydrocarbons	Raw fractions	Sulfurized fractions after removal of aromatic hydrocarbons
200-300	-	-	0.2	0.2
300-350	-	-	0.5	0.4
350-400	-	-	0.8	0.8
400-450	2.2	2.2	1.5	1.4
450-500	3.8	3.7	3.0	2.0
500-550	2.9	2.6	-	2.2



and low molecular weight aliphatic hydrocarbons. In the simplest case, this process may be shown by the following equation:



The calculated change in free energy for this process at 25°C is 2,760 cal., and the reaction is thermodynamically possible. The initial cyclohexane has a density of 0.7781 g/ml, while the new system composed of aromatic and aliphatic hydrocarbons has a computed density of 0.6558 g/ml, the possibility of contraction being neglected. Thus, the transformation of 3 gram-moles of cyclohexane into 1 gram-mole of benzene, 1 gram-mole of hexane and 2 gram-moles of propane will cause a decrease in density of 0.1223 g/ml. The decrease in the density of the initial system becomes even more evident when the redistribution of the elements proceeds to completion, namely, to the formation of graphite and methane



In this case, the change in the free energy per gram-mole of cyclohexane is 36,324 cal.; i.e., the reaction is quite possible and will proceed practically to the end. The volume of the initial system of 1 gram-mole of cyclohexane is 108 ml, while the volume of the new system composed of graphite and methane, and containing the same amount of carbon and hydrogen by weight (84 g), is as high as 67,220 ml; i.e., the density of the system has decreased by a factor of 622.

Similar conclusions may be drawn from examination of any other thermodynamically possible reaction in any series of hydrocarbons. Inasmuch as all these reactions consist essentially of redistribution of the elements in the environment of petroleum reservoirs, carbon-enriched compounds accumulate at one extreme and hydrogen-saturated compounds at the other. Any intermediate stage will differ from the preceding one by an increase in the number of molecules in the system; this must lead to a decrease in the density of the system. Any increase in the density of the system because of an increase in the number of condensed molecules composed of aromatic rings is completely compensated by a considerable reduction of density resulting from the breakdown of the system and formation of a large number of new lighter molecules.

Clearly, decrease in density is caused by the disintegration of the system initially composed of a relatively small number of molecules. The system evolves towards an increase in the number of molecules and reflects a general tendency towards the establishment of the most probable state of the system under the action of spontaneous processes.

Basically, the specific gravity of petroleum

depends on three variables: a) the proportion of different fractions and especially the content of the light benzene fractions, b) the particular hydrocarbon series of which the petroleum is composed and c) the content of asphaltic substances.

Quantitatively, the influence of the first factor is more important than of the other two. Inasmuch as the transformation of the petroleum hydrocarbons is from the complex molecules to the simplest, i.e., to paraffins, monocyclic naphthenes and aromatic hydrocarbons, it results in the increased content of the low boiling point fractions such as benzene and kerosene. The breakdown of the complex molecules does not occur all at once but through a sequence of stages. The heavy molecules break down into relatively large fragments, and these, in their turn, into smaller ones. As a result, at a definite stage of transformation the molecules constituting the intermediate boiling point fraction of petroleum are formed, then the kerosene molecules, and finally, at the end of the process, the benzene molecules. For this reason, the naphthene-base oils of the intermediate stage of transformation are rich in the fuel [?] oil and kerosene fractions but are poor in benzene. As the transformation of petroleum continues, the intermediate fractions change to benzene and their content decreases. For example, Groznyy petroleum yields very little fuel [?] oil and kerosene, but a great deal of benzene and ligroin; the last two substances are not at all characteristic of the naphthenic oils from Baku.

The specific gravity of petroleum decreases with depth under normal conditions of transformation. However, precise regularity of this kind is possible only if the petroliferous strata are sufficiently uniform and the effect of secondary processes negligible. The reverse relationship between specific gravity and depth is occasionally observed (Bibi-Eybat, the Lenin region of Apsheron Peninsula and some other localities).

There are also localities where the specific gravity gradient changes at random from positive to negative, the specific gravity alternately increasing and decreasing with depth. In such cases it must be assumed that the character of contact between the petroleum and the enclosing rocks changes or that external factors have affected the transformation trend towards paraffinization. Although the specific gravity of petroleum may be regarded as a criterion of the degree of its transformation, the decrease in specific gravity with depth must be taken as a statistical relationship only. Statistically, the deviations in one direction or the other cancel each other and the relationship becomes a general law.

Geologic age must be regarded as a probability factor. All other conditions being equal,

the greater the geologic age of the reservoir rocks, and therefore the older the petroleum, the greater the probability of the occurrence of regular and energetically justifiable processes of decomposition of molecules characterizing the transformation of petroleum.

Noteworthy in this connection are the statistical data on the characteristics of the world oils from the different geological formations published by G. A. Amosov (1952), G. P. Tamrazyan (1954), and V. A. Uspensky and O. A. Radchenko (1947). The data compiled by these investigators are presented in Table 4.

TABLE 4. Average characteristics of petroleum from different geologic systems after G.A. Amosov (1952), G.P. Tamrazyan (1954) and V.A. Uspensky (1947)

Age of reservoir rocks	Specific gravity		Average sulfur content, percent	Average paraffin content, percent	Benzene yield, percent	Kerosene yield, percent	Specific rotation, $[\alpha]_D$
	Average	Weighted average					
Cenozoic	0.886	0.888	0.67	1.9	19	17	1.00
Mesozoic	0.875	0.872	0.49*	3.1	21	12	0.35
Paleozoic	0.842	0.848	0.48	4.1	26	15	0.26

\*Weighted average

It is clear from this tabulation that the geologically old petroleum is much richer in paraffins and are, in general, more strongly transformed. The ancient Paleozoic petroleum has lower specific gravities and contains more of the benzene fraction than the younger Tertiary and even Mesozoic oils.

#### RATIOS OF NORMAL HYDROCARBONS OF THE PARAFFIN SERIES TO THEIR STRUCTURAL ISOMERS

Investigation of the ratios of the normal hydrocarbons to their isomers in petroleum is a very important but, unfortunately, still little developed phase of the geochemistry of petroleum. It is very probable that these ratios might serve as indicators of the depth of its transformation.

It is known that normal paraffins have higher free energy than their structural isomers (table 5).

A number of important conclusions may be drawn from an examination of the free energies of the isomers in the aliphatic series presented in Table 5. The change from the normal members to the structural isomers with one methyl group in the side chain is accompanied by a substantial reduction in free energy. Further isomerization with the appearance of new methyl groups also causes decrease in free energy, but by a somewhat smaller amount. The diminution in free energy does not continue indefinitely with the addition of new methyl groups, but stops

in each isomeric series after a certain definite number of groups has been added. In hexanes and heptanes the decrease in free energy ceases with the appearance of two methyl groups; in octanes, with the appearance of three groups.

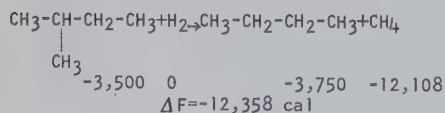
The position of the methyl group is also significant; the nearer it is to the end of the chain, the lower the amount of free energy in the hydrocarbon. The free energy of an isomer with two methyl groups attached to one carbon atom in the molecule is less than of an isomer with two methyl groups attached to separate carbon atoms.

TABLE 5. Standard free energies of compounds,  $F^0_{2980K}$  after V.V. Korobov and A.V. Frost (1949), M.F. Nagiyev (1950) and others

Formula	Compound	Free energy cal/mole
$C_5H_{12}$	n-Pentane	-1,960
$C_5H_{12}$	2-Methylbutane	-3,500
$C_5H_{12}$	2, 2-Dimethylpropane	-3,640
$C_6H_{14}$	n-Hexane	+50
$C_6H_{14}$	3-Methylpentane	-510
$C_6H_{14}$	2-Methylpentane	-110
$C_6H_{14}$	2, 3-Dimethylbutane	-950
$C_6H_{14}$	2, 2-Dimethylbutane	-2,350
$C_7H_{16}$	n-Heptane	+2,090
$C_7H_{16}$	3-Methylhexane	+1,100
$C_7H_{16}$	2-Methylhexane	+980
$C_7H_{16}$	2, 4-Dimethylpentane	-720
$C_7H_{16}$	3, 3-Dimethylpentane	+630
$C_7H_{16}$	2, 2-Dimethylpentane	+90
$C_7H_{16}$	2, 3-Dimethylpentane	+160
$C_7H_{16}$	2, 2, 3-Trimethylbutane	+760
$C_8H_{18}$	n-Octane	+4,140
$C_8H_{18}$	With one branch	+3,000
$C_8H_{18}$	With two branches attached to different carbon atoms	+2,500
$C_8H_{18}$	With two branches attached to one carbon atom	2,500-3,000
$C_8H_{18}$	With three branches, two attached to one carbon atom	3,000-4,000
$C_8H_{18}$	With four branches 2, 2, 3, 3-tetramethylbutane	+4,880

Conclusions important to the study of the transformation of petroleum may be drawn from these facts. For example, it is more probable that normal hydrocarbons will change into hydrocarbons with methyl groups than vice versa. It must be understood that the formation of each new methyl group in a molecule, the number of carbon atoms remaining the same, amounts essentially to redistribution of hydrogen, so that the hydrogen atoms originally uniformly distributed through the molecule become concentrated about one of the carbon atoms, while another carbon atom becomes impoverished in hydrogen. The accumulation of methyl groups in molecules resulting from spontaneous processes was noticed long ago by Butlerov, Flavitsky and Favorsky; A. F. Dobryansky (1937) observed that the same effect was produced by the thermal metamorphism of hydrocarbons. Recently this phenomenon was discussed by M. S. Reznichenko (1955), who called it the "law of accumulation of methyl groups" in chemical reactions.

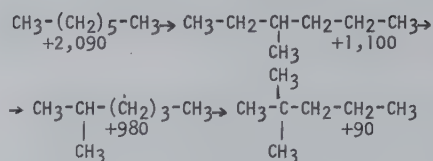
This phenomenon acquires a much more general significance when considered from the thermodynamic point of view as an indicator of the degree of transformation of the organic molecule in the process of decrease in its free energy. It is natural to assume that structural isomerism of a normal hydrocarbon molecule accompanied by accumulation of methyl groups is only the first step in the process of lowering its free energy. After the molecule has accumulated the maximum possible number of methyl groups, further lowering of free energy must be effected by some other process, and the only possible process is the separation of the methyl groups in the form of methane formed with the aid of hydrogen freed as a result of inter-system redistribution from other, mainly aromatic molecules. No other process can lower the free energy level in the initial system.



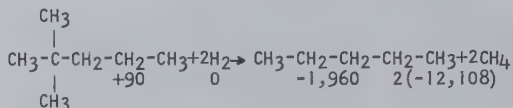
As a result of separation of methane, normal hydrocarbons once again appear in the system, but with a smaller number of carbon atoms. If more than three carbon atoms are present per molecule, these hydrocarbons will again form isomers with side chains, until all possibility of isomerization of a given molecule is exhausted.

The following thermodynamically possible reactions may occur:

### 1. Isomerism of heptane.



2. Separation of two methane molecules from isoheptane.

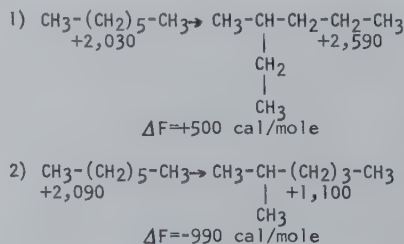


The total decrease in free energy as a result of isomerism and separation of two molecules of methane is 28,266 cal/mole. The hydrogen needed for the final stage of transformation of 2, 2-dimethylpentane into pentane is produced by the dehydrogenation of the aromatic and, in part, of naphthene hydrocarbons, which occurs in the system simultaneously with this transformation.

Other sequences of reactions may be pictured for transforming heavier paraffins into lighter ones by isomerism and separation of methane groups.

It should be noted that the mechanism of these reactions explains well the predominance of methane over ethane in petroleum. Ethane and methane have very similar vapor pressure; and if petroleum were subjected only to the processes which lead with equal probability to the formation of either of these gases, the natural gases would contain like amounts of each. Actually, however, methane always predominates over ethane in natural gases.

The ideas developed here provide an easy explanation of this. The point is that isomerization of a normal paraffin can produce only a small amount of an isomer with the ethyl radical because energetically this is less advantageous than the formation of the methyl radical.



The positive change in the free energy in the



first reaction and the negative in the second indicates that the second reaction is much more probable than the first. Therefore, formation of isomers with the methyl radical is much more probable in the aliphatic series than of isomers with the ethyl radical. This causes preferential formation of methane and is reflected in the composition of the non-condensing petroleum gases. Thus, in the system composed of paraffins every moment of time is marked by disappearance and reappearance of normal hydrocarbons as well as by appearance and disappearance of their structural isomers.

The decomposition of a substituted cyclic compound leads to the formation of a branched carbon chain. Such a radical cannot isomerize into a normal chain but can only separate from the ring as a branched structure. If, however, in some way or other, the formation of a normal radical becomes possible, this relatively simple act or isomerization will cause lowering of the free energy of a molecule as a whole; this process of isomerization is, therefore, not only possible, but inevitable, provided that the number of carbon atoms in the side chain is not less than four. Naturally, the shorter radicals will separate exclusively, as the simplest hydrocarbons have no isomers. Thus, the new paraffin radicals forming as the result of decomposition of ring compounds will be most probably of the normal type. The paraffinic radicals formed by opening of cycles are most likely to be isomeric.

It is probable that under these circumstances branched paraffins must predominate during the initial stages of transformation of petroleum, and only in the later stages will normal paraffins appear in the system, but with lower molecular weights.

At every moment of time the petroleum hydrocarbon system will contain very complexly

interrelated normal and isomeric hydrocarbons. The higher hydrocarbons are not readily accessible to direct study, and in our present state of knowledge we can consider only the ratios of structural isomers in the lighter petroleum fractions, the ligroin and kerosene.

The predominance of branched paraffins in the light fraction of a given petroleum indicates that it has undergone transformation at relatively shallow depth. On the other hand, accumulation of light paraffins with normal structure indicates a greater depth of transformation.

Data on the content of isohexane in different petroleum are given in Table 6. The petroleum are placed in two groups, the first of which includes the relatively light paraffin oils of Pennsylvania and Second Baku; the second, the heavy, slightly transformed petroleum of California, Emba and some other localities. The first group is characterized by the predominance of normal hexane over its isomers. The content of n-hexane is, on the average, 60 percent of the total hexane present, while its four possible isomers account for only 40 percent. The average content of the isomer with a Quaternary carbon atom, 2,2-dimethylbutane, is the least, only 1.5 percent, and the average ratio of n-hexane to 2,2-dimethylbutane is 40.

Different ratios are found in the little transformed, heavy asphaltic oils. The average content of n-hexane in them is much lower (24.5 percent), but the content of its isomers is much higher. The content of 2,2-dimethylbutane rises to 5.5 percent of the total hexanes, and the ratio of n-hexane to 2,2-dimethylbutane is 4.

These ratios of the hexane isomers in the different types of petroleum agree with the thermodynamic considerations given above. In the primary, little-transformed petroleum the

TABLE 6. Percentage of hexane isomers in straight-run ligroins from different petroleum. After Rossini (1957) and Kazansky and Plate (1953).

Locality	n-Hexane	2-Methylpentane	3-Methylpentane	2,3-Dimethylbutane	2,2-Dimethylbutane
Greendale, Kawkawlin, Michigan	81.5	9.2	6.3	2.7	0.3
Ponca, Oklahoma	68.5	14.1	13.0	3.0	1.4
Eastern Texas	50.0	25.0	19.0	4.2	1.8
Bradford, Pennsylvania	49.0	29.0	17.2	3.5	1.9
Surakhany (lubricant fraction)	51.2	20.6	20.6	5.1	2.5
Tuymazy (Devonian)	60.1	21.7	17.0	0.0	1.2
Average	60.0	20.0	15.5	3.0	1.5
Conroe, Texas	43.2	28.1	19.5	5.7	3.5
Midway, California	35.8	32.2	21.4	5.8	4.8
Winkler, Texas	14.6	21.6	54.2	6.7	2.9
Surakhany (select)	14.3	39.2	14.0	25.0	7.5
Koschagyl	13.2	33.8	24.8	18.1	10.1
Average	24.5	31.0	26.8	12.2	5.5

# INTERNATIONAL GEOLOGY REVIEW

branched compounds predominate over the normal. They form during the early stages of transformation by the opening of rings and separation of side chains. The following stages are characterized by the separation of methyl groups from the branched paraffins as a result of conjugate hydration and formation of the main mass of normal members of the aliphatic series.

We have reviewed the data on the content of the hexane isomers only, but the data for other hydrocarbons confirm our conclusions. Table 7 presents the composition of the hydrocarbons

The relationship is reversed in the light paraffin oils of Oklahoma, Michigan and Pennsylvania, in which normal paraffins predominate strongly over branched paraffins. However, here also the role of branched paraffins in the group composition of the light distillates is very considerable.

Table 8 gives similar data for five samples of Soviet oils.

In this case the composition of fractions boiling below 150°C is examined. These fractions are much more difficult to separate into

TABLE 7. Group composition of straight-run 40°-102° ligroins from American petroleum, in percent. After Rossini and others (1957).

Hydrocarbon series	Greendale, Kawkawlin, Michigan	Ponca, Oklahoma	Eastern Texas	Bradford, Pennsylvania	Conroe, Texas	Midway, California	Winkler, Texas
Normal paraffins	62.2	35.3	24.6	34.1	17.6	9.9	9.5
Branching paraffins	13.0	20.2	27.1	32.0	19.6	21.4	61.4
Alkylcyclopentanes	7.8	23.1	25.9	13.4	16.6	40.7	20.4
Alkylcyclohexanes	15.5	20.2	21.9	20.0	42.6	27.4	8.2
Benzenes and alkylbenzenes	1.5	1.2	0.5	0.5	3.6	0.6	0.5
Total	100.0	100.0	100.0	100.0	100.00	100.0	100.0

in the 40°-102°C ligroins, obtained by direct distillation from the same petroleum whose content of the hexane isomers was examined above. In this case, also, the quantitative relations between the normal and side-chain paraffins are rather clearly apparent.

In the heaviest naphthene petroleum of Texas and California the branched paraffins strongly predominate over the normal paraffins. This is especially clear in the case of petroleum from Winkler, Texas, in which isoparaffins amount to 61.4 percent and the normal paraffins to only 9.5 percent.

components than the light petroleum fractions, and for this reason a considerable percentage falls into the undifferentiated category. Table 8 shows rather clearly that branched paraffins predominate over the normal in the Surukhan naphthenic oils and the heavy Koschagyl oil of the Emba region. In the Devonian Tuymazin petroleum, transformed at a greater depth, the content of the normal paraffins is rather high and they predominate over isomeric paraffins.

We have reviewed here only a few regularities in the composition of petroleum as functions of their transformation, basing our dis-

TABLE 8. Group composition of straight-run ligroins distilled from some Soviet petroleum at temperature below 150°C, in percent. After B.A. Kazansky and A.F. Plate (1953).

Hydrocarbon series	Kazanbulak	Tuymazy (Devonian)	Surakhany (lubricant fraction)	Koschagyl	Surakhany (select)
Normal paraffins	21.0	30.4	17.0	5.6	2.0
Branching paraffins	11.1	36.8	19.9	16.6	13.4
Alkylcyclopentanes	5.2	5.4	14.6	18.3	18.2
Alkylcyclohexanes	21.3	11.6	29.0	34.7	43.0
Benzene and alkylbenzene	5.1	5.2	3.5	2.8	0.9
Undifferentiated	36.3	10.6	16.0	22.0	22.5
Total	100.0	100.0	100.0	100.0	100.0

cussion on thermodynamic analysis of the probability of a given reaction and on actual analyses of petroleum. We did not touch on such previously established regularities (Dobryansky, 1948) as the increase in the amount of light fraction distillates with stronger transformation, or the accumulation in the oil of large amounts of methylbenzene and the increase of the simplest aromatic hydrocarbons in this benzene. This account does not include all of the regularities known at present; they are undoubtedly much more numerous and their number will grow as our knowledge of the composition of petroleum increases.

# REFERENCES

- Amosov, G. A., 1952, Issledovaniye opticheskogo vrashcheniya neftey [INVESTIGATION OF OPTICAL ACTIVITY OF PETROLEUM]: Abstract of dissertation, VNIGRI, Leningrad.
- Andreyev, P. F., 1957, Energeticheskiye osnovy organicheskoy teorii proiskhozhdeniya nefti [ENERGETICS OF ORGANIC THEORY OF ORIGIN OF PETROLEUM]: Geokhimicheskii Sbornik, VNIGRI, no. 4, Gostoptekhizdat.
- Bogomolov, A. I., and Indenbom, F. B., 1951, Opyt geokhimicheskogo issledovaniya neftey mestorozhdeniya Kulsary Yuzhno-Embenskogo rayona [GEOCHEMICAL INVESTIGATION OF PETROLEUM FROM THE KULSARY OIL FIELD IN THE SOUTH EMBA REGION]: Geokhimicheskii Sbornik, VNIGRI, no. 2-3, Gostoptekhizdat.
- Danilov, S. N., and Danilova, E. D., 1956, Molekulyarnyye peregruppirovki i vnutrimolekulyarnyye okisleniye-vosstanovleniye. Sbornik "Reaktsii i metody issledovaniya organicheskikh soyedineniy", vyp. 4. [MOLECULAR REGROUPING AND INTERMOLECULAR OXIDATION-REDUCTION". In the book: REACTIONS AND METHODS OF INVESTIGATION OF ORGANIC COMPOUNDS, no. 4]: Goskhimizdat.
- Dobryansky, A. F., 1937, Nauchnyye osnovy krekninga nefti [SCIENTIFIC BASIS OF THE CRACKING PROCESS]: ONTI.
- \_\_\_\_\_, 1948, Geokhimiya nefti [GEOCHEMISTRY OF PETROLEUM]: Gostoptekhizdat.
- Favorsky, A. E., 1928, Reaktsiya odnovremennogo okisleniya i vossatnovleniya i izomernyye prevrashcheniya [SIMULTANEOUS OXIDATION AND REDUCTION REACTIONS AND ISOMERIZATION]: Journ. fiz. -khim.
- \_\_\_\_\_, 60, p. 369.
- Kartsev, A. A., 1954, Geokhimicheskaya klassifikatsiya neftey [GEOCHEMICAL CLASSIFICATION OF PETROLEUM]: "Azerb. neft. khoz.", no. 3.
- Kazansky, B. A., and Plate, A. F., 1953, Issledovaniye individual'nogo sostava benzinov. Trudy vsesoyuznogo soveshchaniya po khimii i pererabotke nefti [INVESTIGATION OF INDIVIDUAL COMPONENTS OF BENZENES. TRANSACTIONS OF ALL UNION CONFERENCE ON CHEMISTRY AND REFINING OF PETROLEUM]: Izd. Azerbaijan Academy of Sciences, Baku.
- Korobov, V. V., and Frost, A. V., 1949, Svobodnyye energii organicheskikh soyedineniy [FREE ENERGIES OF ORGANIC COMPOUNDS]: Moscow.
- Nagiyev, M. F., 1950, Termodinamicheskiye raschety protsessov pererabotki nefti i dannyye po svoystvam khimicheskikh soyedineniy [THERMODYNAMIC CALCULATIONS OF THE PROCESSES OF OIL REFINING AND DATA ON THE PROPERTIES OF CHEMICAL COMPOUNDS]: Gostoptekhizdat.
- Oakwood, T. S., 1952, OPTICAL ACTIVITY OF PETROLEUM. Ind. Eng. Chemistry, vol. 44, no. 11.
- Rossini, F. D., 1960, CHEMICAL THERMODYNAMIC PROPERTIES OF HYDROCARBONS, CRUDE OILS. Oxford University Press, New York.
- Rossini, F. D., Mair, B., and Streiff, A., 1957, Uglevodorody nefti [PETROLEUM HYDROCARBONS]: Russian translation. Gostoptekhizdat.
- Tamrazyan, G. P., 1954, K voprosu o periodichnosti v izmenenii kachestva neftey v razreze otlozheniy ot del'nykh tektonicheskikh etapov razvitiya zemli [PERIODICITY IN THE VARIATION IN QUALITY OF PETROLEUMS IN SECTIONS OF DEPOSITS OF DIFFERENT TECTONIC STAGES]: Doklady Akademiyi Nauk SSSR, t. 99, no. 3.
- Teznichenko, N. S., 1955, O zakone nakopleniya metil'nykh grupp [THE LAW OF ACCUMULATION OF METHYL GROUPS]: Sbornik nauchnykh rabot Leningr. instituta torgovli, no. 9, p. 96.
- Uspensky, V. A., and Radchenko, O. A., 1947, K voprosu genezisa tipov neftey [ON THE PROBLEM OF ORIGIN OF DIFFERENT TYPES OF PETROLEUM]: Gostoptekhizdat.



# EXPERIMENTAL STUDIES OF COMBUSTION IN OIL SANDS<sup>1</sup>

by

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• translated by Royer and Roger, Inc. •

## ABSTRACT

Experiments on combustion in oil sands permit the determination and clarification of the combustion mechanics in oil-sand layers and the extraction of oil. To a considerable extent the problems of composition requirements of fuel within the mixture are clarified. A description of these fuels and the rate of movement in the combustion zone are presented. The various technical achievements of a given process are not the sole bases of these conclusions, however, it should be mentioned that the thermal process of combustion extraction is not a universally adaptable method, as a sufficiently permeable layer is necessary. It also requires relatively heavy oil which does not completely saturate the pore space. Moreover, the sand must be relatively free of water or ignition is completely impossible.

A series of questions still have to be answered relative to such aspects as the lithological composition of the layer, the gas content, the thickness of the layer, the quality of the oil, and the speed of oxidation. --Author's conclusions.

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## INTRODUCTION

There are two main categories of thermal methods of oil extraction. The first is the process of obtaining oil by utilizing surface heat; the second method is ignition of oil in the strata. For the latter process, data are necessary to determine the conditions of combustion within the oil-bearing strata (sand, sandstone); as, for instance, the equilibrium conditions of the combustion front, its rate of movement, temperature gradients, the optimum content of the ignited fraction, the influence of water, oxidizing agents, etc.

The following experimental studies are intended to clarify some of these problems.

### OIL-SAND MIXTURES AS MEDIA FOR COMBUSTION

Oil-sand mixtures are self-sufficient combustion media. They consist of a large amount of neutral particles of sand and a combustible oil fraction, which is widely dispersed and distributed throughout the surface area of the sandstone.<sup>2</sup> Thus, the customary concept of liquid fuel is not adequate here. On the other hand, an analogy to solid fuel is also insufficient. This mixture is not actually a consolidated skeleton of ash cemented by a combustible fraction, as is the case in coal or shale. The ash content in

oil-sand mixtures is quite different from any form of fuel. If in fuels ranging from wood to oil shales the ash content is from 0.5 to 64 percent and coal with 20 percent ash content is considered low-grade, then the oil-sand mixture (5-15 percent oil content by weight in ratio to dry sand) would have an ash content of 95-85 percent. Furthermore, if we recall that no more than 2.5 percent of the oil is combustible, then the ash fraction is still further increased, and the heat-producing fraction which is ignited in the combustion zone can develop only up to about 250 kcal/kg. Thus, certain doubts arise concerning the possibility of controlling oil combustion in a porous medium. Experiments have shown, however, that there is no basis for such doubts. They have revealed the possibility of using stable combustion of oil-sand masses for the purpose of extracting oil. A. B. Sheinman and others (1935, 1954), experimenting in the laboratory and under natural conditions have shown that an oil-bearing sandstone layer can be ignited, and the combustion within it can proceed through the layer in a uniform front, with the aid of an airflow.

Kuhn and Koch (1953) have conducted experiments in the laboratory which have proved that oil and sand can be ignited even with water present, and that the combustion proceeds in the form of a slowly moving front within a confined thickness until wind motion is introduced. Koch and Gleason (1954) have conducted experiments under natural conditions which show that oil-sand mixtures can be ignited, and that the combustion front can move through the sand.

Hester (1954), Grant and Szasz (1954), and Smith and Watson (1953) have shown, from experiments conducted under natural conditions, that the coke residue in a sand can be ignited and will burn in a stream of air or other gas containing oxygen.

<sup>1</sup> Translated from *Eksperimentalnoye issledovanie goreniya v sloye neftenosnogo peska*: Trudy instituta nefti, Akademiya Nauk SSSR, v. 11, 1958, pp. 228-239.

<sup>2</sup> The immersible surface area of grains having a diameter of 0.01 mm is 445,000 m<sup>2</sup> per m<sup>3</sup> of rock.

## INITIAL MATERIALS

Combustion was conducted in various media: quartz sand mixed with oil or asphalt residue, natural oil-bearing sandstone, and sand with admixtures of coke and coal. A stream of air was used as an oxidizing agent.

Lyuberetsky sand-quartz sand without any clay fraction. Fractional composition: 0.5-1.55 percent, 0.5 ÷ 0.25-64.38 percent, 0.25 ÷ 0.15-25.06 percent, 0.15 ÷ 0.09 - 0.0 percent, 0.09-8.58 percent.

Kirmakinsky sand - natural oil-bearing rock, compact, dense and cemented with petroleum residue of a cinnamon-brown color. Oil content (after extraction) was 4-6 percent by weight. The oil extracted during the experiments was thick, acidic and asphaltic.

Il'skaya oil - b. p. 275°C, specific gravity 0.9147, residual fraction up to 300° - 10 percent, the viscosity  $\eta_{100}=3.23$ .

Residual asphalt - residue of Tuimazinsky asphalt, insoluble in propane-butane fraction. Boiling point 345°C, specific gravity 1.0336, residual fraction above 500° - 14 percent, and viscosity approximately 800 centipoise.

In order to prepare a natural mixture, 100 parts by weight of sand and 5 parts by weight of oil or asphalt were used.

## EXPERIMENTAL APPARATUS AND EXPERIMENTAL PROCEDURE

The experiments were conducted in a silica glass and metallic apparatus (figure 1). The basic parts of the apparatus are: a cylindrical tube (quartz, diameter 40 mm,  $L=350$  mm  $V=440$  cubic centimeters; and a metallic tube with a diameter of 106 mm,  $L=995$  mm and  $V=8,750$  cubic centimeters), the electric starter for ignition, reservoir for oil, a thermo-couple and a flow meter.

Pipes were filled with the oil-sand mixture, and subjected to specific pressure. The experiment began with the activation of an electric starter for ignition. In three to four minutes, at a temperature 300-350°C (sufficient for ignition), the electric starter was turned off. Air was circulated through the pipe. The further increase in temperature within the layer, (up to 600° and higher) resulted from the oil combustion. The combustion front moved progressively through the layer in the form of a narrow belt in the direction of the oxidation stream. The oil became concentrated in the collecting receptacle. The water formed during the combustion process became either incorporated into the oil, or vaporized. During the experiment temperatures and air pressure were recorded along

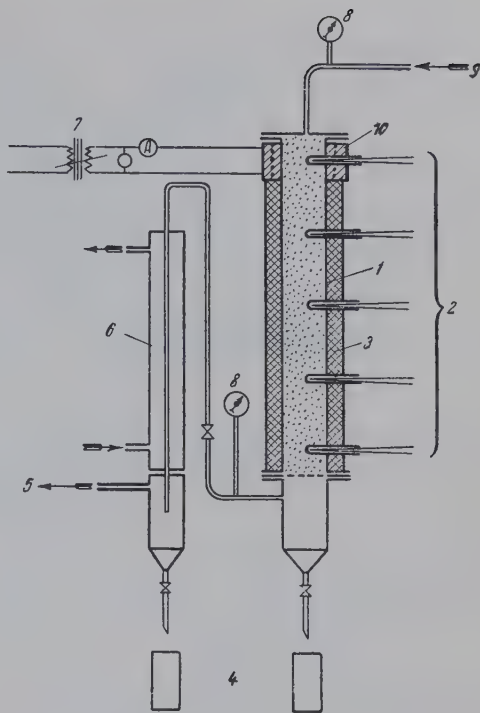


FIGURE 1. Diagram of apparatus  
1) Tube with oil-saturated rock; 2) thermo-couples; 3) heat insulator; 4) reservoirs for oil products; 5) exhaust for gaseous products; 6) cooler; 7) autotransformer; 8) pressure gauge; 9) intake for air coming from the compressor, through the flow meter; 10) electric igniter.

consecutive points on the axis of the tube. The supply of air was kept constant.

## THE GENERAL CONDITIONS OF THE EXPERIMENT

The results of the initial observations are given in Figures 1-9. They represent temperature-time relations (fig. 2), recorded by an automatic galvanometer at different points on the tube. The temperature at different points on the tube increases progressively to a maximum, which is the characteristic temperature for the combustion front at any given point in the pipe (left part of the curve), and then progressively decreases, indicating cooling of the sand by the air flow (right part of the curve). The progressive movement of the temperature maximum is similar for all the points along the tube, and shows that the combustion process at any given instant is regular and controlled. The curves show that the combustion front in an oil-sand layer has the form of a narrow incandescent belt (with a width of 10-15 mm), which moves progressively in the direction of the air stream, occupying the entire cross-section of the tube. The combustion front does not turn back after

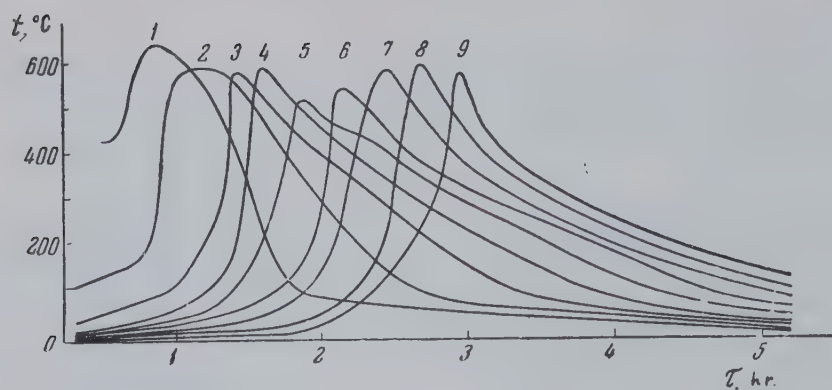


FIGURE 2. Dependence of temperatures on time for the various sections of oil-saturated rock (curves from initial observations). 1 through 9 are numbers of the curves, representing the consecutive sections.

having passed any given point. The combustion front and its movement can be observed directly if a quartz tube is used.

# HEAT WAVES

Figure 3 shows temperature curves from

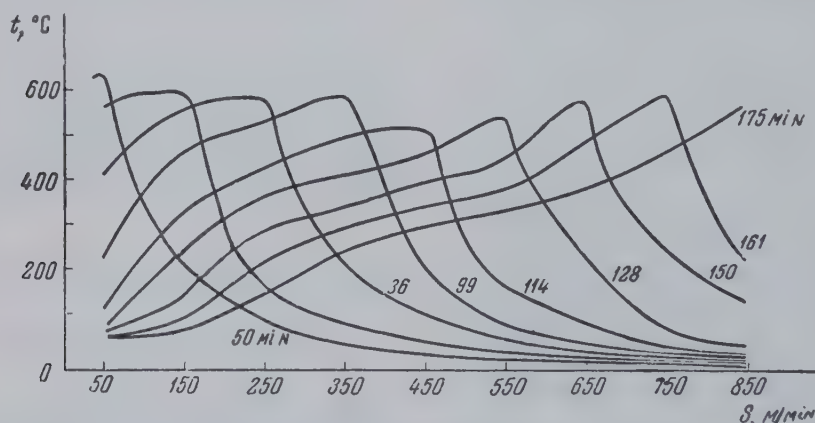


FIGURE 3. Measurement of temperature at the various points in the oil sand, plotted against time.

points  $t-s$  for the time elapsed since the beginning of the experiment. The curves are constructed as a cross section along the vertical axis of Figure 2, for any given time lapse since the beginning of the process. The temperature-distance curves are also similar to each other and, if superimposed on each other, they coincide. The configuration of these diagrams gives a temperature description of the heat wave moving along the tube axis from one point to another at a constant rate.

# THE RATE OF MOVEMENT OF THE COMBUSTION FRONT

The relationship between path and time for

the maximum temperature level of the combustion front is clearly linear in character, (fig. 4), consequently the rate of movement of the combustion front is constant for the whole path. The observed rate of movement of the combustion front is 0.6 - 1 centimeter per minute or 0.35 - 0.6 meters per hour,

under a constant air stream.

In Figure 5 curve no. 1 represents the relationship between the rate of movement of the combustion front and the amount of air supplied; curve 2 describes the relationship between the temperature of combustion and the amount of air used. From the curves (fig. 5) it is apparent that the average active temperature of combustion and the rate of movement of the combustion front have similar maxima. This indicates that the rate of movement of the combustion front is influenced by the combustion temperature. In further experiments, these relationships should be determined



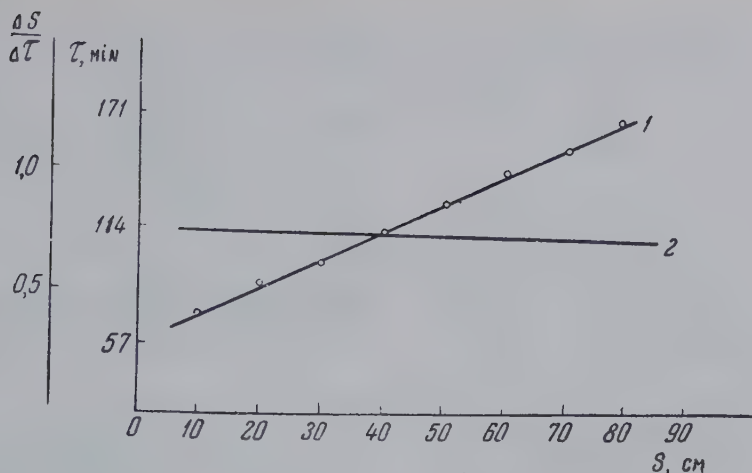


FIGURE 4. Distribution of the combustion front along the oxidation stream in time (1) and rate of movement of combustion front (2).

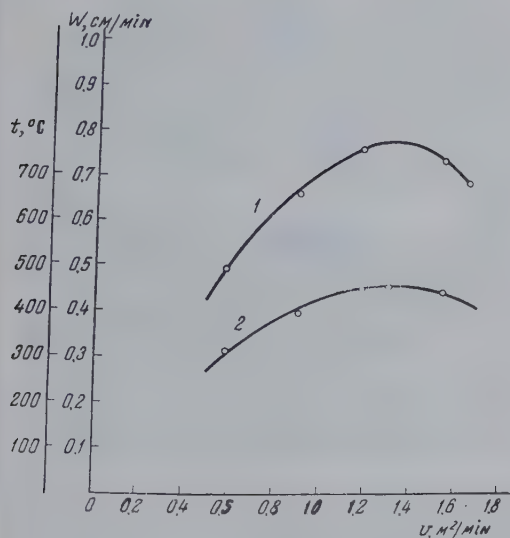


FIGURE 5. The rate of movement combustion front in relation to the specific amount of oxidant expended (1) and the temperature of the combustion front in relation to the specific amount of oxidant expended (2).

together with the constant factors influencing the rate of the front movement.

#### TEMPERATURE RELATIONSHIPS

The temperature relationships in the process are described by the initial curve (fig. 2), and also by the curves of maximum temperature (fig. 6). In the combustion zone, the maximum temperatures are equal to 600 - 700°C. The temperature in the combustion zone diverges imperceptibly from the mean and is maintained at a given level which is concrete indication of the possible control and stability of combustion in the oil-bearing sand layer.

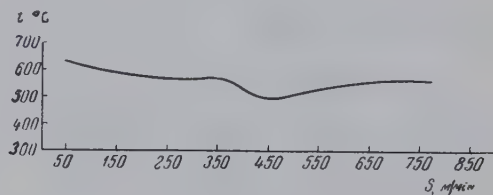


FIGURE 6. Change in the temperature of the combustion front for the various sectors of the oil sand.

The temperature  $t$  in the combustion zone is determined by the temperature balance of the combustion process, and depends on the amount of combustible fuel (coke residue and gas vapor phase), and on the temperature loss in the spaces surrounding the combustion zone in directions perpendicular to the movement of the front. Loss of heat depends on the diameter of the tubes, and is particularly great with small diameters. This should be considered during the evaluation of the experimental results.

#### COMBUSTION AND HEATING

Figures 7 and 8 give data on the rate of temperature change within the layer  $\frac{\Delta t}{\Delta \tau}$  both during the heating and cooling period. At temperatures of 150 - 250°, ignition of the combustible fraction of the oil-sand mixture occurs (figs. 2 and 3). In Figure 7 the curve at this point is sharply deflected indicating a change from a gradual rise in temperature to a transition period, and then a rapid rise at the moment of combustion. Combustion within the narrow front lasts for a short time, after which the temperature at any given point begins to decline, as the combustion proceeds into a neighboring section. The second curve (fig. 8) describes the conditions of heat transfer from the porous medium to the oxidizing agent. The curve

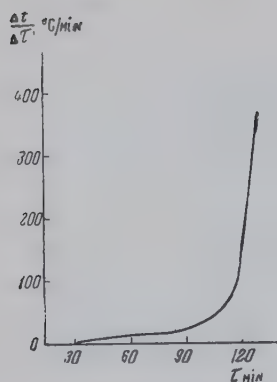


FIGURE 7. The rate of temperature increase in relation to time for the different sectors of oil sand lying in the path of the combustion front.

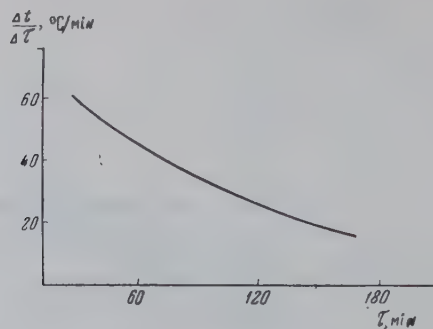


FIGURE 8. Rate of temperature decline in relation to time for the different sectors of oil sand lying in the path of the combustion front.

stretches along the abscissa.<sup>3</sup>

### MECHANISM

The experiment showed that the stable, gradual movement of the high-temperature combustion front in a layer of oil-bearing sand can occur despite the high "ash" content.

This process takes place by a series of consecutive reactions, of which combustion is the last. Preceding it are several thermophysical changes in the combustible fraction, including vaporization, gas formation and coke formation.

The layer of oil bearing sand can be schematically divided into three basic areas during combustion (fig. 9); area I - dry, burned-out

region in which transformation of matter reactions occur. Qualitatively determined, it divides the entire layer into regions I and II which vary in concentration and gas component. On one side we find the empty sand through which the air is passing, on the other the oil-saturated area with a moving flow of combustion vapors.

Examining the combustion area, we can distinguish several consecutive zones which are characterized by various reactions and various states of matter. These zones are shown in Figure 10. The most important role in the combustion process is played by the coked part of the sand. In Figure 11, thin-sections made from the coke-sand mass are shown. Actually, the combustion takes place primarily because

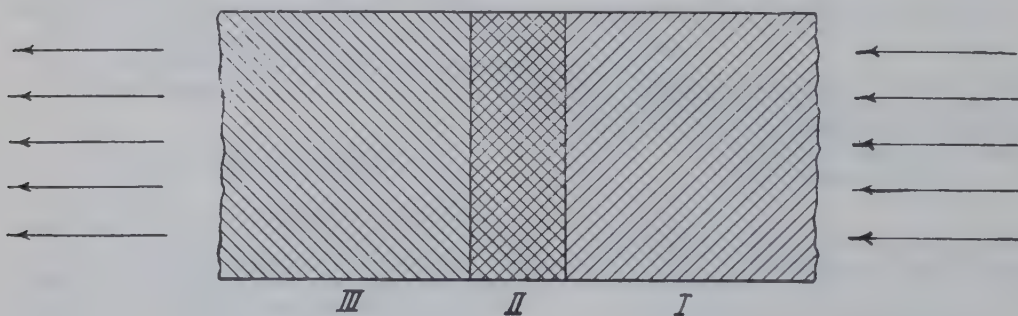


FIGURE 9. Diagram of the distribution of the various sectors along the length of the tube.\*

sand; area II - combustion area; area III - oil-saturated sand. The combustion area is a basic

of the coke which is formed from oil by thermal alteration and distributed on the surface of the sandstone. A second, less important part is played by the vapors and gases. Thus we can say that the combustion of the oil-sand is both a heterogeneous and homogeneous phenomenon, and is accomplished through both diffusional and kinetic processes, which occur simultane-

<sup>3</sup> Curves in Figures 7 and 8 are parts of one general continuous curve and are located for convenience within a normal octant.

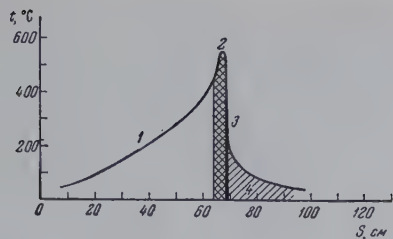


FIGURE 10. Diagram of the combustion front distribution.

1) Rock, free of oil residue; 2) area of combustion; 3) coke and gas formation zone; 4) vaporization zone; 5) oil-saturated sand.

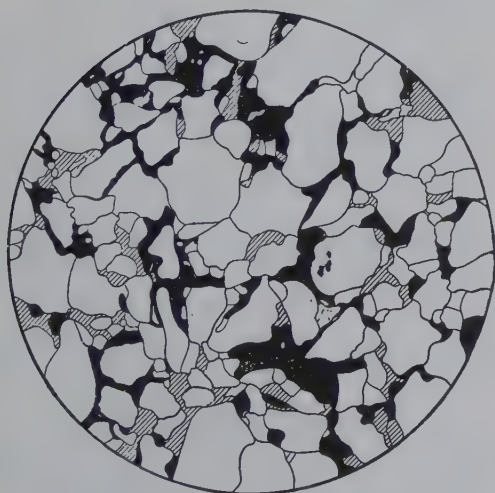


FIGURE 11. Thin section of combustion zone.

● Coke residue; ● pores; ○ grains.

ously. The mechanism of combustion of oil-sand mixtures can be represented in the following way: as the sandstone, surrounded by an oil film, is heated, moisture is generated and vaporization of the light oil fractions and the formation of gases due to cracking and pyrolysis occurs. These light hydrocarbons, upon ignition, form a combustion zone near the grains.

After the generation and combustion of volatiles, which are released, the coke remains. It is sufficiently heated to burn in the atmosphere of the oxidizing agent. The incandescent combustion of the volatiles becomes transformed into a nonincandescent combustion of the basic coke fuel. Moreover, the combustion of the coke does not occur after the escape of the volatiles; the two phases somewhat overlap each other.

The pores of the rock can be considered as independent "jets" from which there is constant generation of the incandescent mixture formed from the oil product and the oxidizing agent.

This mixture becomes ignited when the necessary concentration and temperature are reached. The smaller spaces in their own way create favorable hydrodynamic conditions for the stabilization of combustion fronts.

#### THE NECESSARY AMOUNT OF FUEL

Experiments have shown that with a 10 percent oil content in a mixture, a moving combustion front would consume 10 - 15 percent of this amount, which would equal approximately 1.0 - 1.5 percent of the weight of clean sand. Part of the fuel is burned in the gaseous state, while the other is burned as coke, which has formed from the oil which was distributed on the surface of the grains. An analysis of coke-coated sand has shown that it contains 0.8 - 1 percent of coke of the total weight of dry sand. During combustion in a quartz tube, with 0.9 percent coke content it was impossible to stabilize the process. However, an addition of coal dust into the mixture, giving a total combustible fraction of 2.5 percent and higher, facilitated the formation of a uniform and steady combustion front. This can be clearly seen from the curves of our initial observations given in Figure 12. This steady

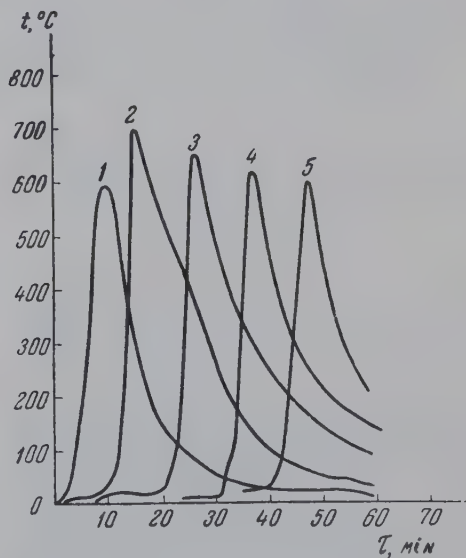


FIGURE 12. Curves for the initial observations during experiments with coked quartz sand, mixed with coal dust to the amount of 2.5 percent of the total weight. 1 through 5 curves, corresponding to the measuring stations along the tube.

and characteristic process can be obtained during the combustion of a quartz sand mixture containing powdered coal (without oil).

In Figure 13 we have shown the curves for the initial observations obtained during the combustion of Kirmakinsky natural oil sands, con-



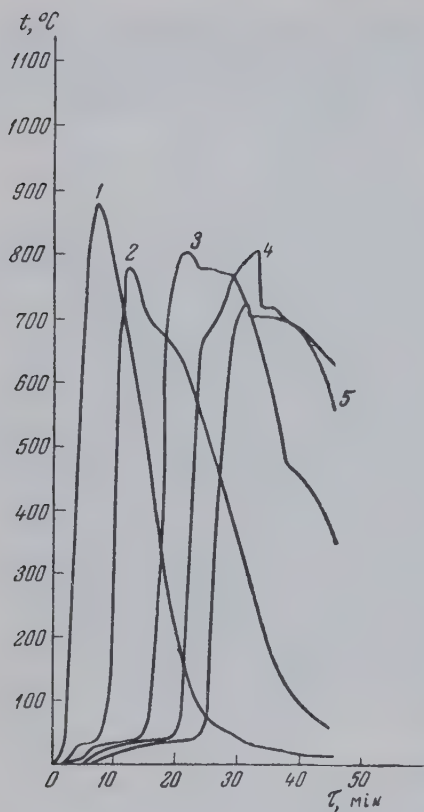


FIGURE 13. Curves for the initial observations during experiments with Kirmakinskii sand. 1 through 5 curves, corresponding to the measuring stations along the tube.

taining 6 percent of heavy acidic oil. Two percent of the oil was burned. The process was accomplished uniformly and steadily.

During combustion of the sand mixture using Ilsky oil the process also proceeded steadily and uniformly. Fourteen percent of the oil mixture was burned (1.4 percent of the total weight with a 10 percent saturation). Thus, the minimum amount of fuel necessary for the control of combustion in a porous medium, with the presence of an air stream, is equal to about 1.5 - 2 percent of the total weight of sand. A larger fuel fraction intensifies the process and makes it possible to obtain higher temperatures in the combustion zone. A fuel fraction greater than 2 percent of the total weight of sand assures stable functioning of the process.

The coke residue assures stability and the continuation of combustion of the oil-sand mixture. It is for this reason that the formation of this residue plays such an important role in the successful functioning of this operation.

On the other hand, insofar as the formation of cokes depends to a large extent on the content of asphalt and tar components in the oil fraction, the oil pools with heavy asphalt-tar oils seem to be best suited for the use of thermal processes which involve the combustion method of extraction. However, this does not necessarily exclude the possibility of combustion extractions from pools with lower tar content. The qualitative application of combustible gases and oxides as oxidizing agents allows the utilization of this process.

For oil pools containing light oils which vaporize at temperatures lower than those necessary for development of a combustion front, it is necessary to adapt other variations of the thermal process.

### THE HEAT BALANCE

The heat balance can be expressed by the following equation:

$$Q = Q_{por} + Q_{nf} + Q_{gz} + Q_{pot} + Q_{rkts}$$

where  $Q$  is the heat generated during combustion of the oil fraction. This is the basic factor of heat generated during the process. Correspondingly,  $Q_{por}$ ,  $Q_{nf}$  and  $Q_{gz}$  are the amounts of heat in the sand, oil and gas, heated as a result of the process.

Thus, all heat absorbed by the rock is re-sorbed by the air flowing through the layer, carrying it into the combustion front in the form of physical heat. After the passing of the combustion front, the burned-out sand does cool. The heated oil and gas of combustion also conduct heat to the adjoining oil-saturated layer. In the final stage of the process, when the heated oil and gas are driven to the surface  $Q_{nf}$  and  $Q_{gz}$  should be also included in the heat loss;  $Q_{pot}$  indicates the amount of heat lost into the adjoining layers. Supposedly this heat, as well as the heat  $Q_{por}$ , is regenerated during transmission of the air stream through the layer. Finally,  $Q_{rkts}$ , is the heat expended during decomposition, coking, vaporization, lowering of viscosity, reaction with the rock, i.e., the physicochemical phenomena connected with the process. This heat is the basic factor in the process, and cannot be regenerated.

Thus, theoretically, one can say that all the heat obtained during the combustion of oil in a layer is expended only on the fuel being extracted and, consequently, the coefficient of heat of a given process where  $Q = Q_{rkts}$ , in the absence of any other loss of heat, that is

$$Q_{por} + Q_{nf} + Q_{gz} + Q_{pot} = 0,$$

is equal to unity. From a practical point of

view, this does not hold true; insofar as the losses will be all directed toward the surrounding rock, the escape of heat with the oil and gas is possible, and as is also quite apparent, part of the heat will remain in the rock. Under laboratory conditions, it has been impossible to obtain a substantial degree of efficiency.

Experiments have shown that the loss of fuel during burning is equal to (5-10 percent for sand) 10 - 20 percent of the bituminous matter in rock, under minimum saturation which is equal to 1 - 2 percent of the total weight of the sand.

### THE PRODUCTS OF THE PROCESS

A representation of the mechanism of oil separation during this process is based on the results of experiments and visual observations. Thermal decomposition (cracking, pyrolysis, gasification) takes place only in the layer directly adjoining the combustion zone. The greater part of the oil is heated to a temperature which facilitates its easy flow through the mineral skeleton. The flow begins at temperatures of 40-50°, and slowly increases with increase in temperature and filling up of pore spaces.

The movement of oil along the layer takes place mainly as a result of the pressure created by the air stream, and the gases of combustion and decomposition. If we examine the layer under high temperatures it is clear that the completely burned-out light sand is directly changed by the coking phase, which moves through the layer filled with different types of asphalt, then through the heavy oil, and then through the fluid oil fraction. These layers correspond to zones which we have indicated during examination of the mechanism of combustion. The products of the process utilizing the combustion method of extraction are gas and oil. The gas has the following composition (percent):

CO-4, CO<sub>2</sub>-6, O<sub>2</sub>-12, H<sub>2</sub>-1.5,  
C<sub>n</sub>H<sub>2n-1</sub>, C<sub>n</sub>H<sub>2n 2</sub>, -1.02, N<sub>2</sub>-74.5,

which indicates the intensity of combustion and thermal decomposition.

The main product is liquid oil. During the processing of sands, we obtained 81 - 85 percent of the original quantity from the Iulsky oil, from asphalt sands, 73 - 71 percent asphalt; from the Kirmakinsky sandstone, 47 - 50 percent of the original oil content. One should keep in mind that both the amount of oil products found in the sand mixtures (high viscosity), and the insignificant initial content (5-16 percent) by weight, would indicate a particularly strong adhesion to the rock, and thus would be almost completely incapable of being separated by other means (water, gas). The sand becomes com-

pletely clean, dry and free from organic remains after the process.

### THE OXIDIZING AGENT

The oxidizing agent can be supplied in the form of air, oxygen, oxygen-enriched air, or a mixture of oxygen (or air) with illuminating gas. This last oxidizing agent in particular would cause some changes in the process since, together with the oxidizing agent, supplementary fuel in the form of gas is introduced into the combustion zone. This gas in less-favorable situations can serve as a stabilizing agent for the combustion front. According to the paper by Smith and Watson (1953), experiments performed on this variation gave favorable results under natural conditions. Experimental works have shown that, though the introduction of pure oxygen facilitates the intensification of the process, it nevertheless causes this setback: it simultaneously decreases the volume of gases introduced into the combustion zone which serve as transporting agents in the mechanism of the process. Due to the flow pressure of the oxidizing agent, the separated oil flows towards the oil well and is concentrated in the shaft. A decrease in the amount of the agent will partially decrease the effectiveness of the dynamic factor, so important in the activity of thermal conditions. Naturally, it is not feasible to increase the dynamic factor by increasing the amount of oxygen.

[Ed.: The "Conclusions" of the original constitute the abstract of this translation].

### REFERENCES

- Grant, F. B., and Szasz, S. F., 1954, *Journal of Petroleum Technology*; May, p. 23-33.
- Hester, D. V. and Menzie, D. E., 1954, *Petroleum Engineer*, November, p. 82, 87-92.
- Koch, R. L., Gleason, J. F., Jr., and Boston, W. G., 1954, *Oil and Gas Journal*, December 6, vol. 53, no. 31, p. 102-106.
- Kuhn, C. S. and Koch, R. L., 1953, *Oil and Gas Journal*, August 10, vol. 52, no. 14, p. 92-96, 113-114.
- Sheinman, A. B., Dubrovai, K. K., Sorokin, N. A., Charygin, M. M., Zaks, S. L., and Zinchenko, K. E., 1935, *Opyty po podzemnoy gazifikatsii neftyanykh plastov v prirodnykh usloviyakh* [EXPERIMENTS IN UNDERGROUND GASIFICATION OF OIL STRATA UNDER NATURAL CONDITIONS]; *Neftyanoye Khozyaistvo*, vol. 4, p. 1-14.
- Sheinman, A. B., and Dubrovai, K. K., 1954, *Podzemnaya gazifikatsiya neftyanykh plastov i termicheskii sposob dobychi nefti* [UNDERGROUND GASIFICATION OF OIL STRATA

AND THE THERMAL METHOD OF OIL EXTRACTION]: ONTI-NKTP.

Smith, R. , and Watson, 1953, Oil and Gas Journal, August 24, vol. 52, no. 16.



# GEOLOGY AND TECTONICS OF THE KUZBAS<sup>1</sup>

by

P. M. Gorshkov

## ABSTRACT

A brief summary of the geological history and structural elements of the Kuznetz coal basin is given. The coal beds overlie Tournaisian limestones and were deposited in a gradually subsiding graben, which existed until the end of the Paleozoic. Continental deposition commenced in the Mesozoic and has continued to the present. Coal reserves in the Kuznetz basin have been estimated at 400 billion tons. --M. Russell.

\* \* \*

In this region (Kuznetsky Alatau, Salair-sky Ridge, Kuznetsk syncline) we have an almost complete Paleozoic cross-section -- from the Cambrian to the Permian. The distribution of Jurassic and Tertiary deposits is very insignificant.

The Carboniferous and Permian deposits are of utmost importance since they contain all of the Kuzbas coal reserves. They are chiefly sandstone with interbedded conglomerates, argillaceous shales, limestone and coal. This uniform producing layer of Carboniferous and Permian attains a thickness of 8 km and is divided into seven formations from horizon to horizon. The coal reserves, estimated at the colossal figure of at least 400 billion tons, are quite well known in the U. S. S. R.

A brief geological history of the basin follows:

The evolution of the Kuznetsk depression is associated with the formation of the surrounding mountain ridges which consist of Cambrian and Silurian rocks. The Salairsky Ridge, due at least in part to folding, emerged from below sea level as early as the Silurian period and, in some places, Cambrian. The same may be said of the Kuznetsky Alatau on the basis of observations on its northwestern slope in the vicinity of the Siberian Railroad. In other words, by the beginning of the Devonian, the Salair and Kuznetsky Alatau already existed as small islands or peninsulas in the vast Ural-Siberian Sea. At the beginning of the Carboniferous the sea shores were extended somewhat with an outlet through a strait at Tomsk.

After the deposition of the limestones of the Tournaisian series, an abrupt change took place

in the physical-geographic conditions, which is reflected in the nature of the deposits: at the bottom a thick stratum of conglomerates was formed alternating with sandstones, etc. -- the beginning of the deposition of the coal-bearing beds of the Kuzbas.

At the same time orogenic processes both in the Altay, here and further north, occurred with new intensity, resulting in the almost complete formation of the Gornyy Altay, Salair and Kuznetsky Alatau. It was precisely this existence of a fringe of large mountain massifs which caused the change in facies of the deposits in the Kuznetsk depression.

The coal basin, with frequent fluctuations in level and outline, existed until the end of the Paleozoic, after which there occurred in it an accumulation of shallow-water and littoral deposits comprising a thick series of coal-bearing deposits. The continental period was established here with the beginning of the Mesozoic and continues into the present.

Orogenic processes occurred repeatedly in the areas surrounding the Kuznetsky depression and it, in varying degrees, has been subject to the same deformations. The structure of the coal-bearing deposits, at least on the periphery of the Kuznetsk Basin, is very closely associated with those phenomena which occurred and were manifested with maximum intensity on its fringes and the bordering mountain ridges.

The principal structural elements of the Kuzbas are:

1. The general shape of the Kuzbas (a long parallelogram) is determined to a considerable degree by the two main, almost mutually perpendicular strikes of the folds -- SE-NW and SW-NE. These two directions are the predominant strikes of folds in the coal bearing formations.

2. In an almost uninterrupted series of deposits, beginning with the Cambrian deposits constituting the outer areas and ending with the Permian deposits in the central part of the

<sup>1</sup>Translated from *Gravimetricheskaya syemka Kuzbassa i Gornoy Shorii* 1931, Part 2, *Geologiya i tektonika Kuzbassa: Akademiya Nauk SSSR, Trudy Soveta Po Izucheniya Proizvoditelnykh Sil, Seriya Kuzbasskaya*, Issue 1, 1932, p.6-8.

Kuznetsk depression, there is observed a continual decrease in the area of distribution proceeding from the older to the younger deposits.

3. Taking the various cross-sections of the basin, we obtain, generally speaking a large synclinal valley (brachysyncline) with a steep, then gradual, then normal, then reversed dip of the sides which, in plan, corresponds to an almost enclosed depression.

4. The fourth principal element characterizing the folding of the coal-bearing formations is the weakening of both folded and disjunctive dislocation for the periphery (from the mountain ridges) to the center of the basin. Generally speaking, the shape and position of the folds are varied. Steep, gradual, and nearly flat anticlines and synclines of folds are observed which are normal, overturned or recumbent. Along with normal folds there are complex folds, the limbs of which are, as it were, "corrugated" with secondary folding. The central part of the basin is characterized by gentle undulations, the outer parts by sharp and frequent "corrugation" in cross-section and plan.

5. Almost all investigators consider the Kuznetsk depression a graben; that is, a sunken portion of the earth's crust surrounded by mountain ranges, the Kuznetsky Alatau and the Salair, which are horsts. As the Cambrian and Silurian deposits within part of the present

mountain ridges of the Salair and Kuznetsky Alatau emerged to the surface, the subsequent history of the evolution between depressions belongs within the framework of the latter. Thus, the lateral ridges of the syncline are in the nature of a framework of folding. Regardless of whether the depression is considered a graben or a geosynclinal type of depression, it must be kept in mind that its subsidence occurred over a very long period of time and not simultaneously in various parts.

6. The Kuznetsk depression is separated from the Salair by an unbroken series of more or less parallel, equally large disturbances with the result that there is observed a certain gradation of the orography and, in places, a lamellar structure. Probably the same can be said of the Kuznetsky Altai (Yavorsky and Butov, 1927, p. 120) ("The Kuznetsk basin with its flanking lateral ridges is included in a region of intense deformation and uplift of the earth's crust with the greatest surface and sub-surface folding, large faults, etc. Therefore, for proper understanding of the structure of the Kuznetsk Basin, further detailed investigations of its border are necessary").

## REFERENCES

- Yavorsky, V. I., and Butov, P. I., 1927, Kuznetsky kamennougolnyy basseyn [THE KUZNETSK COAL BASIN]: Trudy Geol. kom., Nov. Ser., no. 177.

# FEASIBLE NEW METHODS OF PROSPECTING AND EXPLORATION<sup>1</sup>

by

N. G. Zhilkin

• translated by Eugene A. Alexandrov<sup>2</sup> •

(Summary of award-winning papers submitted in competition to the

Ministry of Geology and Conservation of Mineral Resources of the U.S.S.R.)<sup>3</sup>

## ABSTRACT

The Ministry of Geology and Conservation of Mineral Resources, U.S.S.R., announces the winners of its May 1956 contest for the best papers on improved prospecting methods for hidden ore deposits, and methods developed for prospecting specific areas for specific minerals. The top eleven award-winning presentations include: 1) a program of placer prospecting in the Soviet northeast incorporating vertical electric sounding, 2) a program for prospecting buried hydrothermal vein deposits in the Soviet northeast, 3) a method of in-place radioactive-ore prospecting, 4) a method of prospecting for non-placer gold by spectral analysis, 5) directional-drilling in exploring salt-dome structure, 6) a method of soil analysis in geochemical prospecting for mineral halos, 7) a portable plant for taking placer-prospecting samples, 8) improved exploratory methods in molybdenite deposits, 9) an improved method of prospecting deep vein deposits, 10) a three-dimensional seismic prospecting method for subsurface structure, and 11) a method for estimating groundwater reserves in karst and highly fractured areas. --M. Russell.

\* \* \*

In decisions of the 21st Congress of the Communist Party of the Soviet Union, special emphasis was placed on increasing the economic efficiency of geologic exploration through introduction of improved methods of exploration, new drilling techniques and geologic equipment.

Enormous sums of money are spent each year in the Soviet Union for exploration, conducted for geologic study of the country. The primary task facing the country's exploration geologists is to reduce the cost per ton of mineral discovered. At present, it is very important to reduce to the minimum the time necessary for prospecting and exploration of mineral deposits, first of all in petroleum, natural gas, and iron ore. This will allow us to solve the problem of rational distribution of new industrial plants under favorable economic conditions.

Shortcomings during prospecting and exploration reduce efficiency with respect to time and expenditures. Different rational methods of prospecting are still not sufficiently utilized. Specific geologic and structural features of the deposits are not taken into consideration during selection of one or another method, or complex of prospecting methods. The best methods of prospecting and exploration are not always known to the majority of geologists. Much information accumulated during the study of a series of deposits is not properly utilized, processed, generalized nor analyzed. Another

shortcoming is that the best-available equipment is not always utilized.

For the purpose of increasing the economic efficiency of exploratory work the Minister of Geology and Conservation of Mineral Resources of the U.S.S.R. announced on May 19, 1956, a contest for the most feasible propositions and research bearing on the following basic problems:

1) Establishment of a feasible complex of prospecting methods as applied to specific regions and different mineral deposits.

2) Elaboration of new methods of discovering deposits which have no outcrops.

3) Basic improvement in methods of exploration and sampling of mineral deposits.

Competition continued for two years and attracted the attention of many geologists. Geological offices, trusts, expeditions, field parties, as well as individuals, submitted 69 entries.

The suggestions presented were examined by highly qualified specialists.

The judges of the competition were Chairman B. N. Yerofeyev, Vice-Minister of Geology and Conservation of Mineral Resources of the U.S.S.R.; P. S. Burdyugov, Vice-Minister of Geology and Conservation of Mineral Deposits of the U.S.S.R.; N. A. Belyayevsky, member of the Board of Ministry of Geology and Conservation of Mineral Resources; V. M. Kreiter, professor, doctor of geological and mineralogical sciences, and others. They recognized the following as best:

1. Projects by geologists of the Northeastern Geological Administration -- "Methods of

<sup>1</sup>Translated from "Ratsional'nye metody poiskov i razvedki (po materialam konkursa MGION SSSR)." Sovetskaya Geologiya, v. 2, No. 10, October, 1959, pp. 146-152.

<sup>2</sup>Columbia University.

<sup>3</sup>All-Union Research Institute of Mineral Resources.



Prospecting and Exploration of Gold Placers in the Northeast of the U.S.S.R.," and "Method of Vertical Electric Sounding as Applied to Study of Recent Unconsolidated Deposits with a Low-Temperature Permafrost Layer." Both projects were considered as one complex project, and awarded first prize. (Authors: V. G. Bulychev, I. E. Drabkin, S. D. Rakovsky, I. N. Skorina, V. N. Starovoytov, M. I. Suvorov, V. A. Titov, Yu. N. Trushkov, A. G. Tyshinsky, V. S. Yusupov and N. V. Sivkov.)

The authors' method of studying a region involves a consecutive order of investigation, beginning with a small-scale geologic survey, as a rule accompanied by panning of alluvium samples along the stream system, and general evaluation of the region and separate parts of the region for planning more detailed exploration.

A geomorphological survey is conducted on prospective areas, usually on 1:50,000 scale in combination with geophysical exploration using vertical electric sounding. This method allows determination of the thickness of unconsolidated deposits, their lithologic composition and genetic types, and establishment of the location of the ancient stream channels covered by the younger unconsolidated overburden. The combination of the geomorphological survey with electric sounding allows necessary data to be obtained for detailed study of Quaternary geology and geomorphology of the region. This also greatly helps in correct selection of the line to be taken in prospecting and exploration and their organization. Further, on the basis of data obtained, exploratory cross-sections are plotted by a selective method. The purpose of these cross-sections is to discover possible placers.

Next, a plan for preliminary exploration is drawn, consisting of a rational combination of drilling and exploratory pits. An improved technique of percussive drilling used by the authors was very efficient. Increased use of drilling overdigging of exploratory pits resulted in a saving of over five million rubles in 1957. During exploration, vertical electric sounding at the exploratory pits and boreholes is used.

It was possible to discover relics of ancient stream systems in wide watershed areas by geomorphological studies in combination with vertical electric sounding. High-grade gold placers were discovered later along these buried stream systems. This method enabled the discovery of buried placers on the slopes of valleys which have an asymmetrical profile.

Application of vertical electric sounding, under the conditions indicated, reduced exploration costs per kilometer of the profile from 40 to 45 percent. Introduction of this method of prospecting gold placers, proposed by the authors, allowed the Northeastern Geological

Administration to reduce expenses for exploration of placers during 1957 by 30 percent.

2) Works by I. E. Drabkin, B. B. Yevangulov, N. I. Safronov, V. N. Starovoytov, V. A. Titov, V. S. Yakupov and L. M. Skorokhodov: "Method of Prospecting and Preliminary Exploration of Blind Hydrothermal Vein Deposits in the Northeast U.S.S.R.," and "Method of Inductive Recording in Prospecting and Following Along Blind Bodies" (both projects considered as one complex proposition) were awarded the second prize.

The authors offered a system of geological prospecting and exploratory methods efficiently applied since 1954 under conditions in the northeast U.S.S.R. The system includes the following types of works: a) regional geological survey and prospecting on the scales 1:500,000, 1:200,000 and 1:100,000, accompanied by analysis of panning samples taken in the valleys of the drainage network; metallometric, and sometimes magnetometric, land survey; b) detailed geological prospecting and prospecting-exploratory work on the scale 1:5,000, 1:10,000 and 1:25,000, including a geological survey of the ore-bearing areas on the scales 1:5,000 and 1:2,000, sampling of heavy minerals from stream alluvium (especially of creek beds, gullies, ravines, etc.) and on slopes, detailed metallometric survey, geophysical methods (electric prospecting, sometimes with magnetic prospecting), and excavations (ditches, sinking of exploratory pits and drilling of boreholes). All methods of prospecting, including the geophysical and exploratory, are put into effect on the basis of a thorough geologic analysis. Samples on the slopes are taken from small, shallow pits following the contour line, starting at the lower reaches of the valley. The distance between the lines along which the pits are located is from 40 to 150 meters, and the distance between the pits is 20 to 40 m.

Maps of dispersion halos are prepared on the basis of sample analysis. Some maxima are uncovered by short exploratory ditches, not longer than 20 m. Such a system eliminates the need for many expensive main exploratory ditches. However, they are used within the ore zones with disseminated, nest type, and veinlet type of mineralization, and in greisen zones.

Follow-up of uncovered veins and the search for new veins within the discovered ore-bearing area with known contours is performed by means of the IZh (vein searching) device. Asymmetric profiling ("surface logging") is used to prospect for sulfide deposits. In areas where the overburden contains large boulders, the method of induction recording is applied. The theory of this method was developed by V. S. Yakupov. This method is valuable since it makes it possible a) to work in areas with any kind of overburden, particularly in areas where

deluvium contains large boulders and rubble; b) to conduct the survey on the move with a continuous record of the measurements; c) to prospect efficiently for poorly conducting quartz-ore bodies, as well as ore bodies with good (sulfide veins) and medium (sheltered zones) conductivity; d) to avoid recording of false anomalies due to land form irregularities and lack of uniformity in alluvium, which makes easier and simplifies the interpretation of results; e) to use the equipment of the IZh method, which is simple and reliable in performance, and f) to work during the cold period of the year and to increase the efficiency of labor by 20 percent.

A wide application of geophysical methods in combination with geologic methods drastically reduced the need for surface excavations, the cost per ton of metal being explored, and the time necessary to prepare a tin deposit for mining operations. Many large ore bodies and anomalies were discovered here, while the cost of making each exploratory profile during the prospecting stage was reduced from 17 to 20 rubles.

Creation of a method of induction recording, applied to any type of cover, including snow (with an average efficiency of 100 km of electric profiles per field season and cost of 1,000 rubles per km), allowed the administration to prospect in new, large areas previously inaccessible to investigation.

3. The work by M. B. Shiryayeva, A. G. Grammakov, V. I. Baranov, A. A. Tatarnikov, V. L. Shashkin, B. I. Galkin, V. I. Sharova, I. N. Kalandadze, A. A. Prevo, A. S. Liberman, and M. D. Britayev, "Method of Radioactive Sampling of Radioactive Ores under Conditions of their Natural Emplacement," was awarded a second prize.

This method consists of determining the content of radioactive elements in ore without taking samples, by measuring gamma radiation under conditions of natural ore occurrence in the deposit. This method allows determination of the elements present, with the same precision as channel sampling, directly in the mining works, without the taking of samples for further analysis. This method is technically simple, does not require complicated equipment, is very rapid, is considerably cheaper than the conventional method of channel sampling, and, what is especially important, assures an operational control over the element content in ore.

4. The third award was given to N. I. Safranov, V. V. Polikarpochkin and A. A. Utgof (All-Union Institute of Exploratory Techniques) for the project "Spectral Aurimetric Survey as a Method of Prospecting for Gold Deposits Not Accompanied by Placers."

The method proposed by the authors involves the development of geochemical methods of prospecting for gold deposits containing fine-grained and dispersed gold, and may be applied in a variety of cases.

The application of the method is feasible in the existence of eluvial, deluvial, alluvial and other unconsolidated deposits, particularly those which form from materials in the oxidation zone of sulfide deposits with an economic content of very fine-grained, dispersed gold, recoverable neither by panning nor standard gravitational methods of ore concentration.

The authors have developed a highly sensitive method suitable for field conditions when a great number of soil samples must be analyzed for gold content. The method may be applied in prospecting for gold by metallometric and geochemical methods.

The method consists of leaching gold from a 12.5 gram sample with aqua regia. From this solution, the gold is recovered by using activated coal [charcoal?] which is added in small amounts to the solution. Next, the coal, which has adsorbed gold, is burned. The small amount of ash which forms after calcination is analyzed by the conventional method of spectral analysis of metallometric samples.

This method results in an increase of concentration of gold in the sample by a factor of almost 300, while the results of spectral analysis assure the necessary sensitivity in determining gold in amounts of hundredths of a gram per ton. The method is characterized by the simplicity of chemical operations in preparing and performing the analysis, and allows 50 determinations per shift by one laboratory technician. The method of approximate spectrographic determination of gold in coal ash satisfies the requirements set up in metallometry with respect to evaluation of its content according to the appearance of gold lines in a spectrum of the sample. The method of spectral aurimetric survey is a method contributing to the discovery of new gold-bearing deposits.

5. The third prize was also awarded to D. A. Dosmukhambetov and N. U. Imashev (Kazakhstan) for "Slanting Directional Drilling of Exploratory Wells -- a Rational Method of Exploratory Works for Oil and Natural Gas under Conditions of Salt Dome Tectonics."

A means of exploring for oil and natural gas in salt-dome structures in the Emba basin is offered, by means of slanting wells instead of vertical ones. In this case one slanting borehole may supply data as useful as those obtained from two to three vertical wells. This will result in considerable economy of costs and time in exploration drilling by



reducing the number of boreholes needed to define a given structure.

This also allows prospectors to reduce the number of drilling crews, crews of rig assemblers, and crews engaged in erection of derricks, and to concentrate material and equipment in definite places, reducing to a minimum (under conditions at Emba) the amount of drilling equipment as well as transportation costs. The cost, for example, of rigging and drilling three wells (nos. 9, 10, 11 in Tyulyus district) is 5,128,000 rubles. The cost of rigging and drilling one slanting borehole to obtain like results is not more than 2,205,000 rubles, an economy of 57 percent. As a whole, in the Emba basin there is realized an economy of 52 percent in cost and 47 percent in drilling footage by putting down 21 slanting-directional wells instead of 51 vertical wells.

Introduction of this proposed method of turbodrilling of slanting wells in salt-dome structures at Emba is a basic improvement in petroleum and natural gas exploration.

6. The project of N. I. Dolukhanova and E. A. Kyuregyan (Geological Institute of the Academy of Sciences of the Armenian Soviet Republic), "Soil-analytical Hydrochemical Method of Prospecting for Mineral Deposits," was awarded an incentive prize.

The method proposed by the authors is a variation of metallometric survey. It allows establishment and study of secondary dispersion halos according to the absorbed and adsorbed, and easily soluble components. Study of this halo component is of major scientific and practical interest, especially when the total amount of the element indicator in the medium is insignificant, and for elucidation of the nature of geochemical anomalies according to its relationship with the primary (barren) or secondary (ore-bearing) dispersions.

Observations of halos according to aqueous extracts under conditions of predominant development of friable deposits of glacial origin (or others, genetically alien to the rocks forming the overburden in which the halos are enclosed) may be of particular importance.

The method of soil sampling and hydrochemical survey is not complicated. A network with 200-meter spacing is plotted in prospective areas to determine the boundaries of dispersion halos. In areas of detailed study this network is reduced to 5 or 10 m. At each point the soil is made friable [mixed?] to a depth of 0.2 or 0.3 m and a soil sample of 200 or 300 g. is taken (100 g of soil used for analysis). From this sample an aqueous extract is prepared. The translucent filtrate is used for determination of metals by calorimetric methods, in 50 to 100 milliliters of the filtrate. The determination

of molybdenum is performed by the rhodanide method, copper by the carbamate method, lead by the sulfide, zinc by the dithizone, and iron by the general rhodan method.

The preparation of aqueous extracts under field conditions and determination of elements present is conducted by using a portable field laboratory, also developed by the authors.

The laboratory allows performance in the field of 40 analyses for molybdenum and copper, and 20 analyses for each of the remaining elements, per shift.

The value of the method consists in direct evaluation of the prospective value of the region, speed, simplicity, and low cost of analysis, as well as the fact that it can be easily performed by any geologist.

The method was tested and has been successfully applied by the authors since 1951 during exploration of a group of deposits in Armenia.

7. Work by A. A. Lifshits, P. L. Kallistova, A. P. Bozhinsky, V. I. Davydov (TsNIGRI), "A Portable Plant for Taking Exploratory Placer Samples," was also awarded an incentive prize.

The plant offered by the authors for taking of exploratory gold placer samples is of great practical interest, besides being already introduced for manufacture on an industrial scale.

As is known, the washing equipment, such as pan, screen, and gold washer now used for taking of exploratory gold placer samples is imperfect. They do not obtain reliable data for a correct evaluation of the deposit (the actual amount of metal in samples is higher after washing). The portable treatment plant allows uniformity in treating the samples, assuring greater reliability during exploration. The plant almost entirely mechanizes the work done by gold prospectors.

The plant consists of two principal parts: a drum disintegrator and a centrifugal separator. The heaviest of the separate parts is less than 90 kilograms. The total weight of the plant is 300 kg. The material being sampled is loaded through an intake screen into the disintegrator, where water is added. Gravel is retained in the drum, while the fine-grained material with water passes into the centrifugal separator, and the tailings are discarded. The concentrate as well as the gravel in the drum, is periodically discharged. Two cubic meters of water per hour and three kilowatt-hours of electric power are used for treatment of a 0.25 cubic meter sample per hour. The cost of the plant by mass production is 200 rubles. During 1958 eight plants were manufactured and supplied to the following geological organizations: Yakutzoloto, Lenzoloto, and Amurzoloto. The



authors are continuing their work in perfecting the construction of the proposed plant.

8. The work by V. D. Semenyuk and V. A. Kuznetsov, "Project for Improving Methods of Geologic Exploration in Molybdenite Deposits of Shakhtaminskoye, Davendinskoye, and Klyuchevskoye," was also awarded an incentive prize.

The work is concerned with drawing a basis for the possible increase of distance between the samples in the exploratory network, and is of practical importance and comparative rarity in the field of calculating the required network density for sampling of mineral deposits. In general, this work is of interest as a method of exploring vein deposits of a similar type.

The authors used the following methods in their work: a) comparison of exploration data with data of mining exploration and sampling; b) increase in spacing between the exploratory workings and samples; c) consecutive increase of block size; d) geologic analysis of the morphological peculiarities of ore-bearing veins and the distribution of ore mineral in veins, and e) method of variations statistics.

Analysis of materials allowed the authors to establish that the applied network of ditches, exploratory pits, and shafts in all three deposits assured the calculation of proved reserves ("A" category). However, the reserves were taken into account as outlined ("B" category) and in part as indicated reserves ("C" category), i. e. in this case there was an obvious excess of exploratory work.

For calculating outlined reserves, the basic aim of exploration, the authors, applying the method of juxtaposition, recommend an increase in the spacing between samples of from 3 m to 12 m, with a minimum number of 18 samples per block of 65 m by 45 m.

Under conditions of maintaining possible deviations within 95 percent and the number of samples over 18 per block, the spacing permitted between samples is 11 to 20 m. Distances of 50 to 100 m between ditches, 5 to 10 of them per vein (depending on length of veins), may be accepted during surface exploration. This will reduce by more than twice the general volume of exploratory work. Using geological structural analysis, the authors determine the average and minimum thicknesses and metal content in ore deposits. They present data on the interrelation of thicknesses and metal content according to the outlines and dimensions of the ore shoots.

It is regrettable that the authors do not present practical suggestions concerning the method of additional exploration of deposits under investigation (how to find new veins,

ore bodies which have no outcrop at the surface, how to locate in rational ways the exploratory workings for additional exploration of flanks and deep-seated parts of ore deposits, etc.). The very important conclusion about the expediency and possibility of calculating in the deposits studied reserves of A ( $A_2$ ) category was not made. The quality of work is considerably lowered by the incomplete interpretation of metallometric survey data.

9. A work by V. Ya. Novitsky and S. S. Konkin, "Project of Exploration of Deep Horizons of the Western Vein of Voroshilovskoye Deposit," was awarded an incentive prize.

The purpose of the work is to accelerate the exploration of the deposit at deep horizons, to establish prospective value of the deposit, and altogether to reduce exploration costs. The project gives an idea of the western vein of the deposit and allows us to judge to what extent further exploration of deep horizons of the vein as proposed by the authors is expedient.

The reserves were determined by means of boreholes driven in a fan-shaped pattern from the chambers, which undercut the vein from the side of the hanging wall at different horizons and in different profiles. Indicating the advantages of this method of exploration which assures the reduction of volume of preparatory works and the footage of boreholes, the authors stress that such a method limits the possibility of undercutting the vein at depths below 200 m along the vertical distance from the mouth of the borehole, and results in an excessive density of the exploratory network. They suggest an increase in the spacing of the network from 60 by 60 to 60 by 120 and 150 by 150 m. This results in 5.7 percent and 11 percent deviation respectively during the calculation of copper reserves, being sufficient for exploration of reserves of higher categories. Such methods of exploration allow elucidation of the general conditions of ore mineralization at deep horizons, and also give us the possibility of rationalizing their further exploration.

10. The work by V. D. Zavyalov and E. N. Stolyarova (Ukrneftegeofizika), "Materials on the Methods of Seismic Spatial Sounding as a Mass Scale," was awarded an incentive prize.

A method of spatial sounding on a mass scale is a new kind of aerial survey in combination with the seismic method of reflected waves. By means of this method a general study of deep geologic structures is possible, as well as prospecting for structures which are promising for petroleum but have no surface outcrops. This form of sounding allows determination of the spatial position, dip and strike of each reflecting plane. In this case a three-dimensional problem is solved for each reflecting element and each sounding. According to the

results, a vectorial map is drawn which gives a general idea of the deep tectonic structure. On the basis of this map vertical seismic cross-sections are plotted along conditional profiles. In its turn, a unified structural scheme can be prepared according to these profiles at a conditional horizon.

The method of massed spatial sounding allows observations in areas most favorable for obtaining reflected waves, which ensures considerably more complete seismic material. Direct solution of the spatial problem allows determination of the position, dip and strike of each reflecting plane, while the massed character of observations reduces the amount of casual errors. The method is effective in areas of complicated geologic structure, a region difficult to traverse, and rugged country. This method assures greater maneuverability during field work and is more economical.

The method has been applied since 1954 and is an efficient means of conducting exploration. Eight field parties were using this method. These parties investigated 1,200 square kilometers of the internal zone of the Cis-Carpathian depression, discovered the major Uron-Blazhevskaya structure, which is prospective for petroleum, and studied the complicated Borislav structure in the general tectonic aspect of the region.

11. The work by K. P. Petushkov (Central Ground Water Geological Party, City of Tashkent), "An Economical, Fast and Precise Method of Ground Water Geological Exploration and Calculation of Water Reserves in Fractured and Karst Zones," was awarded an incentive prize.

In this work a method is proposed for exploration and calculation of ground water reserves in fractured and karst zones. The essence of the method consists in calculating dynamic and static reserves of water in fractures and karst cavities according to the level-lowering rate in the water-bearing horizon, as a result of experimental pumping, with discharge exceeding the dynamic reserves. Under these conditions, it is not necessary to determine such data as the transmissibility coefficient, specific yield, radius of cone of depression and calculation of interaction of wells, and distance between experimental-exploratory and producing water wells.

This method was checked in a series of cases in Middle Asia and in Kazakhstan, and demonstrated good results. It can be applied also for evaluation of the degree of water saturation of mineral deposits emplaced in very fractured rocks. Calculation of producing reserves by this method is very important in regions with unfavorable water conditions. This work represents a practical value, and the method

is worth introducing into ground water geological studies during exploration of ground waters and calculation of their reserves under conditions of good permeability and specific yield.

Additional awards were given for the following projects:

12. "Application of Wide Band Equipment for Multiple-Layer Media," by M. K. Polshkov and G. V. Bereza (VNII Geofizika).<sup>4</sup>

13. "Approximate Determination of the Size of an Ore Body According to a Site Opened up by Some Working," by I. P. Kharlamov (Geological Exploratory Party of Monchegorsk).

14. "Method of Reduced Well Pumping," by I. P. Solyakov, V. G. Knertsner, P. S. Bondarenko (Ground Water Geological Party of "Artemuglegeologiya" Trust).

15. "Problem of Selection of a Rational Complex of Prospecting Methods for Metals in the Ural Region," by A. S. Vershinin (Central Urals Party).

16. "Orientation of the Core of Ferruginous Quartzites by Means of Magnetic Variometer," by Z. A. Krutikhovskaya (Geological Institute of the Academy of Sciences of the Ukrainian SSR).

17. "Double-Frequency Method of Charged Body," by Yu. N. Shaub (VITR).<sup>5</sup>

18. "Sampling Device LP-1 for Multiple Taking of Samples from the Borehole," by L. I. Petrachkov ("Baleyzoloto" Trust).

19. "Forecast of Technological Properties of Coals," by V. I. Skok (Kuzbassgiproshakht).

It is regrettable that specialists from such major geological organizations as the Belgorod expedition,<sup>6</sup> the Kustanay trust, and others did not participate in this competition. No projects were presented by the VITR, VIRG,<sup>7</sup> VSEGEI<sup>8</sup>, VIMS<sup>9</sup> and other researchers, on generalization of the enormous experience accumulated in the U.S.S.R., and elaboration

<sup>4</sup>All-Union Geophysical Research Institute.

<sup>5</sup>All-Union Institute of Exploratory Technique.

<sup>6</sup>Iron ore deposits of the magnetic anomaly of Kursk.

<sup>7</sup>All-Union Institute of Exploratory Geophysics.

<sup>8</sup>All-Union Geological Institute.

<sup>9</sup>All-Union Institute of Mineral Resources.

and development of the theoretical principles of further improvement of prospecting and exploration methods. These projects would have had a great practical interest.

A whole program of prospecting and exploratory work according to the seven-year plan (1959-1965) can be successfully fulfilled with less costs under condition of maximum introduction of the most effective complex methods, and most of all, of those methods which were registered by the judges of the competition.

Taking into account the exclusively high importance of elaboration and introduction of

new methods of prospecting and exploration, the Minister of Geology and Conservation of Mineral Resources of the U. S. S. R. announced a new competition for the best projects introduced during the period of 1959-1960.

As reflected by the conclusions of the 21st Congress of the KPSS (Communist Party of the Soviet Union) and the June Plenum of the Central Committee of the KPSS, these projects acquire a special meaning and will ensure a further increase of labor efficiency, reduce the time necessary for exploration, and reduce the costs of prospecting and exploratory works.

All-Union Institute of Mineral Resources (VIMS).



# Reference Section

## RUSSIAN AND EAST EUROPEAN GEOLOGIC ACCESSIONS OF THE LIBRARY OF CONGRESS

This section is devoted to a listing of selected geologic items appearing in the two publications of the Library of Congress; Monthly Index of Russian Accessions, and East European Accessions Index. These lists are intended as a means of indicating to researchers in the earth sciences some of the material most recently available for screening, further review, and translation. For this reason the lists do not include material now, or soon to be, published in English. Emphasis is placed on Russian material; the extent to which items from East European sources are listed depends on the country and language involved.

A major function of the AGI translations program is the screening of foreign literature for material that should be made available to the English-speaking scientist. Researchers who need such material are urged to review these lists and send us their recommendations for consideration by the editors; the translation needs of all geologists will be served better thereby.

-- Managing Editor

### MONTHLY INDEX OF RUSSIAN ACCESSIONS

Volume 13, No, 8

November 1960

#### MONOGRAPHIC WORKS

#### 12. GEOGRAPHY & GEOLOGY

ELISEEV, N. A. [Metamorphism] Metamorfizm. [Leningrad] Izd-vo Leningr. univ., 1959. 414 p.  
[MICROFILM]

GAVRILOV, A. M., and L. V. POPOV. [Hydrology and the national economy] Gidrologia i narodnoe khoziaistvo. Pod red. L. K. Davydova. Leningrad, Gidrometeor. izd-vo, 1960. 182 p.

IAKHIMOVICH, V. L., and O. S. ADRIANOVA. [Cenozoic in the Bashkirian cis-Ural region] Kainozoi Bashkirskogo Predural'ia. Ufa, M-vo geol. i okhrany nedr SSSR.

Vol. 1, Pt. 3. [Southern Ural brown coal basin] Iuzhnoural'skii burougol'nyi bassein. 1959. 296 p.

KALIUZHNYI, V. A. [Methods for studying multiple inclusions in minerals] Metody vyvchennia bahatofazovykh vklucheni' u mineralakh. Kyiv, Vyd-vo Akad. nauk URSS, 1960. 167 p. illus.

KOMPLEKSNAIA IUZHNAIA GEOLOGICHESKAIA EKSPEDITSIIA, 1956. [Transactions of the Southern Geological Expedition, 1956] Trudy. Pod red. I. O. Broda. Leningrad, Gos. nauchno-tekhn. izd-vo neft. i gorno-toplivnoi lit-ry. Leningr. otd-nie.

No. 5. [Geology, and oil and gas potentials of the southern U. S. S. R.; Turkmenistan and western Kazakhstan] Geologiya i neftegazonosnost' IUGA SSSR; Turkmenistan i Zapadnyi Kazakhstan. 1960. 441 p.

KONFERENTSIIA PO RAZVITIUI PROIZVODITEL'NYKH SIL VOSTOCHNOI SIBIRI, 1958. [Geology and mineral resources. Nonmetallic minerals] Geologiya i mineral'no-syr'evaia baza. Nerudnye poleznye iskopaemye. [Trudy konferentsii.] Moskva, Izd-vo Akad. nauk SSSR, 1960. 142 p.

KUZIN, P. S. [Classification of rivers and division of the U. S. S. R. into hydrological regions] Klassifikatsiia rek i gidrologicheskoe raionirovanie SSSR. Leningrad, Gidrometeor. izd-vo, 1960. 454 p.

LEVIKOV, M. L., and E. SH. AZARKOVICH. [Practical work in a course of meteorology, hydrology, and hydrometry] Praktikum po kursu meteorologii, gidrologii i gidrometrii. Moskva, Gos. izd-vo sel'khoz. lit-ry, 1959. 310 p.

SIDORENKO, G. A. [X-ray determinator of uranium and uranium-bearing minerals] Rentgenograficheski opredelitel' uranovykh i uranodержashchikh mineralov. Moskva, Gos. nauchno-tekhn. izd-vo lit-ry po geologii i okhrane nedr, 1960. 114 p.

SOVESHCHANIE PO UNIFIKATSII STRATIGRAFICHESKIKH SKHEM DOPALEOZOIA I PALEOZOIA VOSTOCHNOGO KAZAKHSTANA. Alma-Ata, 1958. [Transactions of the Conference on the Unification of Stratigraphic Scales of the Pre-Paleozoic and Paleozoic in Eastern Kazakhstan. Alma-Ata, 1958] Trudy. Alma-Ata, Izd-vo Akad. nauk Kazakhskoi SSR.

Vol. 2. [Devonian, Carboniferous, Permian] Devon, karbon, perm'. 1960. 253 p.

ZAKAVKAZSKAIA KONFERENTSIIA MOLODYKH NAUCHNYKH SOTRUDNIKOV GEOLOGICHESKIKH INSTITUTOV AKADEMII NAUK GRUZINSKOI, AZERBAIDZHANSKOI I ARMIAANSKOI SSR, 1st. [Proceedings of the First Conference of Young Scientists of the Geological Institutes of the Academies of Science of Georgia, Azerbaijan, and Armenia] Trudy. Erevan, Izd-vo nauk Armianskoi SSR, 1959. 202 p.

#### 13. SCIENCE

AKADEMIIA NAUK SSSR. Geofizicheskii institut. [Problems in the study of varying electromagnetic fields in the earth] Voprosy izucheniia peremennykh elektromagnitnykh poлей v zemle. Moskva, Izd-vo Akad. nauk SSSR, 1956. 93 p.  
(CoBBS)

DINESMAN, L. G. [Changes in the nature of the north-western part of the Caspian Depression] Izmenenie prirody severo-zapada Prikaspiiskoi nizmennosti. Moskva, Izd-vo Akad. nauk SSSR, 1960. 158 p.

KOCHETKOVA, V. I. [First men on the earth] Pervye ljudi na zemle. Moskva, Izd-vo "Znanie," 1960. 36 p. (Vsesoiuznoe obshchestvo po rasprostraneniui politicheskikh i nauchnykh znani. Ser. 12, Bibliotekha sel'skogo lektoira, no. 2)

KOPANEV, I. D. [The Antarctic snow cover] Snezhnyi pokrov Antarktidy. Leningrad, Gidrometeor. izd-vo, 1960. 142 p.

SEMENOV, V. G. [Effect of the Atlantic Ocean on the regimen of temperature and precipitation in the European part of the U. S. S. R.] Vliianie Atlanticheskogo okeana na razhim temperatury i osadkov na Evropeiskoi territorii SSSR. Moskva, Gidrometeor. izd-vo, 1960. 147 p.

VINEBERG, G. G. [Primary production of bodies of water] Pervichnaia produktiia vodoemov. Minsk, Izd-vo Akad. nauk BSSR, 1960. 329 p.

#### 16. TECHNOLOGY

ALIKHANOV, E. N. [Development of the petroleum and the gas industries in Azerbaijan] Razvitiie nefiianoi i gazovoi promyshlennosti Azerbaizhdhana za semiletie, 1959-1965 gg. Baku, Azerneftneshr, 1959. 93 p.  
(MH)

# REFERENCE SECTION

- BERKHMANN, L. L. [New boring equipment] Novoe burovoe oborudovanie. Moskva, Gos. nauchno-tekhn. izd-vo neft. i gorno-toplivnoi lit-ry, 1960. 161 p.
- BESSONOVA, A. S. [Aluminum raw materials of the Irkutsk Province and possible ways to use them] Aluminievye syr'e Irkutskoi oblasti i vozmozhnye puti ego ispol'zovaniia. Pod red. S. I. Beneslavskogo, Irkutsk, Irkutskoe knizhnoe izd-vo, 1958. 41 p. [MICROFILM]
- BIELIAKOV, M. F. [Collection of problems in foundation engineering] Zbirnyk zadach z osnov ta fundamntiv. Kharkiv, Vyd-vo Kharkivs'koho derzh. univ. im. O. M. Gor'kogo, 1960. 183 p.
- BUNCHUK, V. A. [Temperature regimen of reservoirs; applying the theory of heat resistance to the temperature regimen calculation of reservoirs and the development of measures for reducing the evaporation losses of petroleum products] Temperaturnyi rezhim rezervuarov; primeneniie teorii teplostoiichivosti k raschetu temperaturnogo rezhima rezervuarov i obosnovaniu meropriiati po snizheniu poter' nefteproduktov ot ispareniiia. Pod obshchei red. V. S. Iablonskogo. Moskva, Otdel nauchno-tekhn. informatsii, 1958. 189 p.
- KUL'SKIY, L. A., and T. M. ROVINS'KA. [Practical work in the chemistry and microbiology of waters] Praktikum z khimii ta mikrobiologii vody. Kyiv, Derzhbudvydav URSR, 1957. 131 p. (DNLM)
- LEVANTOVSKIY, V. L. [With a rocket to the moon] Raketoi k lune. Moskva, Gos. izd-vo fiziko-matem. lit-ry, 1960. 379 p., illus.
- MELIK-STEPANOV, I. U. G., I. U. SOKHIN, and I. P. STABIN. [New methods of heavy fluid separation and use of magnetic separation in flowsheets for dressing complex ores and placers] O novykh raznovidnostiakh metoda razdeleniia v tiazhelykh sredakh i primeneni magnitnoi separatsii v skhemakh obogashcheniia kompleksnykh rud i rossypel. Moskva, Izd-vo Akad. nauk SSSR, 1960. 35 p.
- MUSHENKO, I. F. [Coal mining in the Chinese People's Republic] Vydobutok vugillia v Kitais'kii Narodnii Respublitsi. Kyiv, Derzh. vyd-vo tekhn. lit-ry URSR, 1959. 126 p.
- [PETROLEUM GEOLOGY; guidebook] Geologiya nefti; spravochnik. Moskva, Gos. nauchno-tekhn. izd-vo neft. i gorno-toplivnoi lit-ry.  
Vol. 1. [Principles of petroleum geology] Osnovy geologii nefti. Pod red. N. A. Eremenko. 1960. 592 p.
- ROBINZON, E. A. [Petroleum in the Tatar A. S. S. R.] Nefti Tatarskoi ASSR. Izd. 2., perer. i dop. Moskva, Izd-vo Akad. nauk SSSR, 1960. 273 p.
- SAIDAKOVSKIY, S. Z. [Engineering geology] Inzhenerna geologiya. Kharkiv, Vyd-vo Kharkivs'koho derzh. univ., 1958. 242 p.

FROM: EAST EUROPEAN ACCESSIONS INDEX LIST

Volume 9, No. 10

October 1960

## BULGARIA

### 12. GEOGRAPHY & GEOLOGY

#### PERIODICALS

TRDOVE vvrkhu geologiiata na Bulgariia. SERIA STRATIGRAFIJA I TEKTONIKA. (Bulgarska akademiia na naukite. Geologicheski institut Sofia. [Papers on stratigraphy and tectonics issued by the Geological Institute, Bulgarian Academy of Sciences]

No. 1, 1960.

Bonchev, E., and others. Bases for the tectonics of the Kraishite and its adjacent land. p. 7.

Spasov, Kh. Stratigraphy of the Paleozoic sedimentary rocks between Trun and Temelkovo, southwest Bulgaria. p. 93.

Tsankov, V., and others. Geology of the Burela region and its adjacent land between Trun and the Village of Slivnitsa. p. 103.

Vrublianski, B. Geology of the Zaburdeto region. p. 133.

Spasov, Kh. Stratigraphy of Ordovician and Silurian in the center of the Svoje anticline. p. 161.

Tsankov, V., and others. Stratigraphic investigation of the Jurassic and Cretaceous periods in northwest Bulgaria. p. 203.

Minkov, M. Loess and loessic sedimentary rock between the Skomlia and Ogosta Rivers. p. 249.

Petrov, P. Geologic and hydrogeological observation around the extinct Kozhukh volcano in southwest Bulgaria. p. 295.

#### 13. SCIENCE

##### PERIODICALS

PRIRODA I ZNANIE. (Bulgarsko prirodizpitatelno druzhestvo) Sofia. [Issued by the Bulgarian Society of Natural Science. Ten no. a year]  
Recurrent feature: Bibliography.

Vol. 12, no. 7, Sept. 1959.

Paskalev, Z. Elementary components. p. 15.

Rushev, D.; Dimitrov, D. Precious minerals. p. 18.

Zafirov, S. Gypsum. p. 21.

Barska, S. Superstitions connected with the minerals. p. 22.

Vol. 13, no. 3, Mar. 1960.

Nikolov, D. Erosion and the struggles against it. p. 16.

Georgiev, M. The geomorphology and neotectonic movement in the Samokov Valley. p. 159.

## CZECHOSLOVAKIA

### 12. GEOGRAPHY & GEOLOGY

DROPPA, ANTON. Demanovske jaskyne a zaujimavosti krasu v okoli. [Vyd. 1.] Bratislava, Sport, 1959. 147 p. [The Demanova Caves, and karst formations in the surrounding area. French, German, and Russian summaries. 55 illus., 5 fold maps in pocket. bibl. tables]

#### PERIODICALS

CASOPIS PRO MINERALOGII A GEOLOGII. (Ceskoslovenska spolecnost pro mineralogii a geologii pri Ceskoslovenske akademii ved) Praha. [Journal issued by the Czechoslovak Society of Mineralogy and Geology, Czechoslovak Academy of Sciences; with English, German, and Russian summaries. Quarterly]

Recurrent features: Biographies; Book reviews; News from the Society.

Vol. 5, no. 1, 1960.

Bernard, J.; Hak, J. Tetrahedrites with a rich content of silver in Kutna Hora, Stara Vozice, and Pribram; investigation of minerals of the tetrahedrite group VII. p. 1.

Brezinova, D. Petrographic investigation of the lignite seam of the Svatopluk Mine in Mydlovary near Ceske Budejovice. p. 9.

Horak, L. Coprolithus salevensis Parejas, 1948, in the Rhaetic limestone in the environs of Sv. Jakub, north of Banska Bystrica. p. 12.

Chlupac, I. A new finding place of Devonian fossil fauna near Ludmírov in the Drahany Highland. p. 15.

Pleinerova-Hladka, N. Remarks on the petrogenesis of the crystalline mantle of the plutonic rocks in the Carlsbad region. p. 28.

Purkynova, E. Some new fossil plant discoveries in the Namurian of the Ostrava region. p. 38.

Trdicka, Z. Occurrence of fluorapatite in the magnesite talc deposit in Samo, in the Slovak Ore Mountains. p. 42.

Petránek, J. Rhythmic sequence of layered rocks and cyclical sedimentation; a contribution to terminology. p. 48.

Watznauer, A. Contributions to the knowledge of variscite plutogenesis; a lecture delivered at the meeting of the Czechoslovak Society of Mineralogy and Geology, Prague Branch, on February 10, 1959. p. 52.

- Fojt, B. Pharmacosiderite in Flouha Ves near Havlickov Brod. p.61.  
Kuchar, J.; Vins, V. A new locality of Culmian fauna in the Drahaný Highlands. p.66.

# Ceskoslovenska společnost zemepisna. SBORNIK.

Praha. [Journal issued by the Czechoslovak Geographical Society; with English and Russian summaries. Quarterly]  
Recurrent features: News; Book reviews; Maps and atlases.

Vol. 65, no. 2, 1960.

- Hurnik, S. Periglacial phenomena at Slatinice south of Most. p.81.  
Brazda, C. Geomorphological conditions of the Mnichov Brook basin in the Carlsbad region. p.95.  
Balatka, B. Potholes in the bed of the Jizera River. p.110.

NEMEC, FRANTISEK. Kluc na urcovanie nerastov. [Prel. a doplnil: Jan Bako. 1. vyd.] Bratislava, Slovenske pedagogicke nakl., 1959. 248 p. [Key for identifying minerals. 1st ed. illus., bibl., footnotes, indexes, tables]

Prague. Ustredni ustav geologicky. VESTNIK. Praha. [Journal issued by the Central Geologic Institute, Czechoslovak Academy of Sciences. Six no. a year]  
Recurrent feature: Book reviews.

Vol. 35, no. 4, June 1960.

- Cepek, L. Fifteen years of free geology. p.261.  
Kodym, O.; Suk, M. Geology of the western part of the Plutonian in Central Bohemia. p.269.  
Rousek, V.; Vrba, J. Conditions in the wider environs of the Teplice nad Jeovou Spa from the viewpoint of engineering geology and hydrogeology. p.279.  
Zeman, J. Megacyclothems in the Ostrava-Karvina District. p.299.  
Stemprok, M. The cross cutting of a quartz-wolframite vein by albite granite in the ore area of Horní Slavkov. p.315.  
Jencek, V. Preliminary report on the character of the crystalline rocks in the northeastern part of the Olesnice anticline. p.319.  
Cadek, J.; Malkovsky, M. Indications of ores, connected with the occurrence of thermal waters in the environs of the Teplice Spa in Bohemia. p.321.  
Masek, J. Rocks of the coal basin of Radnice. p.325.  
Frajova, H. A find of the Lower Cretaceous species *Pseudobelus bipartitus* Blainville, 1827, in the Koprivnice development of the Stramberk limestone in Stramberk. p.327.  
Chlupac, I. Stratigraphy of the Drahaný facial development of the Devonian in Moravia. p.329.  
Elias, M.; Frajova, H. A find of a coral stock enclosed in the tescenite. p.333.  
Knobloch, E. A new finding place of the paleogenetic flora in the Carlsbad region. p.335.  
Hurnik-Luft, S. Contribution to studies of the tectonic conditions of the central part of the southern edge of the Chomutov-Most-Teplice basin. p.337.  
Matejka, A.; Tyrznik, B. In memory of Karl Juttnier; an obituary. p.341.

## 13. SCIENCE

PIRODOVEDNY CASOPIS SLEZSKY. ACTA RERUM NATURALIUM DISTRICTUS SILESIAE. (Ceskoslovenska akademie ved. Slezsky ustav) Opava. [Journal on natural sciences issued by the Silesian Institute, Czechoslovak Academy of Sciences. In Czech and Polish with English, German, and Russian summaries. Title varies: before v.20, 1959, Prirodovedecký sborník Ostravského kraje. Quarterly]  
Recurrent feature: Book reviews.

Vol. 20, no. 2, 1959.

- Kumpera, O. Contribution to the lithology of Bilovec Beds. p.139.  
Vasicek, M. The origin of faunas in cyclothems. p.184.  
Ambroz, V.; Kneblava, V. Glaciation of the Repiste Plateau. p.194.  
Michalek, R.; Pexa, L. A contribution to the knowledge of underground waters in the eastern part of the Ostrava-Karvina coal basin. p.219.

Klir, S. Hydrogeology of the polymetallic ore deposit near Horní Benesov. p.49.

Oberc, J. A tentative interpretation of the transitions between two formations of a different age. Tr. from the Polish. p.79.

Sibrava, V. Sediments of the Saale glacial epoch near Fudnek. p.99.

Kroulik, V. Some microgeomorphologic phenomena in the sandpits around Opava and Krnov. p.111.

Kneblava, V. Report on the 3d Conference of Paleobotany in Krakow. p.232.

Vol. 21, no. 1, 1960.

Havlena, V. The paleontologic relation of the Ostrava beds to the Namurian beds of Western Europe. p.1.

## 16. TECHNOLOGY

### PERIODICALS

CHEMICKE LISTY. (Ceskoslovenska akademie ved.

Ceskoslovenska společnost chemicka) Praha. [Journal on chemistry issued by the Czechoslovak Chemical Society, Czechoslovak Academy of Sciences. Monthly]

Recurrent features: Brief notes; Book reviews.

Vol. 54, no. 6, June 1960.

Kobrova, M. Determination of rubidium and cesium ions in mineral waters. p.564.

RUDY. (Ministerstvo hutního průmyslu a rudných dolů)

Praha. [Publication on ore mining and mineral and ore dressing issued by the Ministry of the Metallurgical Industry and Ore Mines. Includes a supplement: *Práce výzkumných ústavů, papers of the Research Institute of Iron Metallurgy and the Ore Research Institute. Superseded in part Uhli a rudy. See also Uhli. Monthly]*

Vol. 8, no. 4, Apr. 1960.

Vavro, M. Problem of mechanizing roof and bench work while working with the filling. p.113.

Mosna, J. Graphic method of calculating the average thickness of a seam in the course of boring operations. p.119.

Stohl, J. Some problems of rational mining in deposits of ferrous metals. p.122.

Sopko, A. Prospecting, mining, and dressing of uranium ores in the light of the Geneva Conference. p.127.

Soukup, B. Determination of an economical depth in quarrying. p.132.

Kratochvíl, J. Effect of the structure of the production plan and the fixed costs on the level of costs in mining enterprises. p.136.

Benes, M. Accuracy of determining the output of concentrate by weight in metal ore dressing. *Prace.* p.13.

Vol. 8, no. 5, May 1960.

Barcak, A. 15th anniversary of the liberation of mining. p.145.

Kopal, F. Mining in capitalist Czechoslovakia. p.147.

Chovanec, M. Pyritic manganese-ore mines in Chvalětice. p.150.

Faix, A.; Skerlik, I. Results of the fifteen year's activities of iron-ore mines and prospects of their future development. p.154.

Stana, O. Mining development in Bohemia. p.157.

Holko, L. Present problems and prospects of the magnesite industry. p.160.

Pravda, J. Past and future of mining in Moravia. p.166.

Zurav, F.; Paulis, J. Development of Ore Mines in Banská Bystrica. p.169.

Balla, L. Research activities in mining and ore dressing. p.172.

Hynek, A. Planning mines and ore-dressing plants. p.180.

Klir, S. Hydrogeology of the mining area of Chvalětice. *Prace.* p.19.

Vol. 8, no. 6, June 1960.

Zatka, J.; Hrabec, S. New budget system in mines. p.185.



## REFERENCE SECTION

- Schenk, J. Use of machines and equipment devised by the Mine Mechanization Institute for mechanization of mines. p.188.
- Netrval, A. Modern mine with the largest dressing plant in Western Europe. p.194.
- Drawing lode pillars in Mnisek pod Brdy. p.199.
- Pelmar, A. Solution of some problems of magazine mining in Banska Stiavnica. *Prace*. p.27.
- Vol.8, no.7, July 1960.
- Zurek, F.; Kaspar, J. Automation of ore-dressing plants. p.217.
- Soukup, B. Analysis of overhead costs of ore mining. p.225.
- Janak, O. Rationalization and quality in the production of refractory clays. p.229.
- Dvorak, J. Measuring strength in anker bolting by means of string strain gauges. p.234.
- Svoboda, K. Problem of movements of the earth's crust. p.237.
- Zorkovsky, B. Brief survey of occurrence of mineral raw materials in the territory of the Guinea Republic. p.240.
- Vondal, J.; Patera, J. Possible reduction of the consumption of mine timber in mines. p.246.
- Krauter, M. Exploitation of ore deposits in the federation of Malaya. p.248.

## HUNGARY

### 12. GEOGRAPHY & GEOLOGY

- VENDL, ALADAR. Schafarzik Ferenc; a hazai muszaki földtan megalapítója, 1854-1927. Budapest, Tankönyvkiado [1954] 51 p. (Budapesti Muszaki Egyetem Központi Könyvtára. Muszaki Tudománytörténeti kiadványok, 4. sz.) [Ferencz Schafarzik, the pioneer of Hungarian technical geology, 1854-1927. French, German, and Russian summaries. illus., port., bibl.]  
CITY

- VERTES, LASZLO. Untersuchungen an Hohlensedimenten; Methode und Ergebnisse. Budapest, Magyar Nemzeti Múzeum - Történeti Múzeum, 1959. 176 p. (Regészeti füzetek. ser.2, 7.) [Investigations of cave sediments; method and achievements. In German. illus., maps, bibl., diags., graphs, notes, tables]

#### PERIODICALS

- HIDROLOGIAI KOZLONY. HYDROLOGICAL JOURNAL. (Magyar Hidrológiai Társaság) Budapest. [Issued by the Hungarian Hydrologic Society; with English, German, and Russian summaries. Bimonthly]  
Recurrent feature: Development of our terminology.
- Vol.39, no.5, Oct.1959.
- Dr.Gyula Vigh; an obituary. p.325.
- Hartyanyi, L. Investigations into the water household conditions of the model drainage area of internal water in the Kondoros valley. p.326.
- Szigyarto, Z. The annual ice-free high water of the Bodrog River at Bodrogszerdahely and the stage of the Tisza River at Tokaj. p.340.
- Schulhof, O. Application of radioactive isotopes in balneologic research. p.344.
- Grégacs, M., and others. Pollution of the Budapest stretch of the Danube. p.347.
- Dvihalý, Zs. Optical investigations of the Alsogod stretch of the Danube. p.357.
- Urbancsek, J. Ferrous content and hardness of the artesian waters of the Alföld. p.365.
- Vitalis, Gy. Data on the hydrogeology of the Uppony Mountain. p.375.
- Karadi, G. Determination of the seepage losses of irrigation canals. p.381.
- Kovacs, Gy. Checking the relationships suggested for the computation of the distribution of underseepage flow. p.392.
- Beltzky, L. Works related to the exploration of deep waters in the Soviet Union. p.395.

- Vol.40, no.3, June 1960.
- Nagy, I.; G.Karadi. Results of recent investigations into bed-load movements. p.177.
- Szigyarto, Z. Water transportation in ditches alongside roads. p.183.
- Dobos, A.; Szolnoky, Cs. Hydraulic investigation of pump wells. p.185.
- Sebestyen, O. A new system for classifying brackish water; the system of Venice. p.198.
- Fay, Cs. Venturi's proof stick for measuring irrigation water. p.199.
- Szalay, M. Laboratory flow-velocity measurements with spheres. p.204.
- Vitalis, Gy. Geologic possibilities of water storage planned in the area of Salgotarjan. p.208.
- Dziewanski, J. Geologic explorations for the construction of water-power stations. Tr. from the Polish. p.224.
- Leczfalvy, S. Determination of well flow and time of exhaustion of artesian wells. p.227.
- Harmati, I. Chemical analysis of the irrigation and excess waters in the area between the Danube and the Tisza. II. Analyses of the irrigation system of the Algyó Main Canal. p.234.
- Uherkovich, G. Data on the potamophytoplankton of the Tisza River. II. Effect of the Tiszalok Barrage on the algae in the Tisza. p.239.
- Bozsöny, D. Report of the general secretary to the January 21, 1960 General Assembly of the Hungarian Hydrologic Society. p.246.
- Ivicsics, L.; Szigyarto, Z. Conference on Hydraulic Construction held in Brno. p.250.

- NEPRÁJZI KOZLEMENYEK. (Magyar Nemzeti Múzeum. Nepráji Múzeum) Budapest. [Descriptive reports on primary materials in ethnography issued by the Ethnographic Museum, Hungarian National Museum. Four no. a year]

- Vol.4, nos.1/2,3; 1959.

- Szeged, Hungary. Tudományegyetem. ACTA UNIVERSITATIS SZEGEDIENSIS. ACTA MINERALOGICA PETROGRAPHICA. Szeged. [Papers issued by the Mineralogical and Petrographic Institute, Szeged University. In English, German, and Hungarian]

### 16. TECHNOLOGY

#### PERIODICALS

- BANYASZATI LAPOK. (Magyar Bányászati és Kohászati Egyesület) Budapest. [Journal on prospecting and mining issued by the Hungarian Mining and Metallurgical Society. Includes a supplement: *Koolaj*, on crude oil production. Monthly]  
Recurrent features: Foreign news; News from the Society; Book reviews.
- Vol.93, no.6, June 1960.
- Hegedus, F. Important periods, and the production indexes of the development of the Soviet oil industry. p.426.
- Szalai, T. The origin of hydrocarbons. p.430.
- Vol.93, no.7, July 1960.
- Bago, F. Technical and economic effects of the application of steel supports in longwall mining in the Hungarian coal industry. (To be contd.) p.433.
- Toth, G. Determination of granulometry by the Stairmand apparatus. p.444.
- Bán, A.; Lorincz, J. A test of oil recovery on the laboratory model of a reservoir functioning by bottom water pressure. p.495.
- Vol.93, no.8, Aug.1960.
- Bago, F. Technical and economic effect of the application of steel supports in longwall mining in the Hungarian coal industry. p.505.
- Csikó, G. Oil production of the world in 1959. p.553.
- Hortobágyi, I.; Tapolczay, M. The Technical College of Mineral Oil Mining and Deep Boring. p.555.
- Freeman, M. Problems of mining reserves and training of mining engineers in the Anglo-Saxon world. p.574.

Vol. 93, no. 9, Sept. 1960.

- Tarjan, G. Some theoretical problems concerning the classifying and enriching of hydrocyclones. p. 584.
- Ajtay, Z. Safety dam systems in mines for protection against intrusions of water. (To be contd.) p. 597.
- Wein, Gy. Outlooks for prospecting for carbon hard coal in Hungary. p. 604.
- Kiss, L. The new Hungarian bill on mining. p. 630.
- Juratovich, A. Oil-well production equipment in the oil field of Budafa. p. 635.
- Faller, J. Szechenyi and the Hungarian coal mining. p. 646.

**EPITOANYAG.** (Epitoanyagipari Tudományos Egyesület) Budapest. [Publication on the manufacture of building materials issued by the Scientific Association of the Building Materials Industry. Monthly]

Recurrent features: Book reviews; News of the Association; Questions and answers.

Vol. 12, no. 6, June 1960.

- Lehman, H.; Gunter, M. Testing the pouring behavior of suspensions containing clay mineral. Tr. from the German. p. 201.

Vol. 12, no. 7, July 1960.

- Hradsky, J. Trace elements in silicate raw materials. Tr. from the Czech. p. 247.
- Dallendorfer, R.; Langhammer, L. Method for the quick determination of grain distribution in ceramic raw materials. Tr. from the German. p. 251.

**MELYEPITESTUDOMANYI SZEMLE.** (Kozlekedes- es Kozlekedesepitestudományi Egyesület) Budapest. [Publication on civil and construction engineering issued by the Scientific Society of Transportation and Transportation Construction. Monthly]

Vol. 10, no. 7, July 1960.

- Muhs, H. Effect of sandy soil density on building foundations. Tr. from the German. p. 289.
- Bakonyi, F. Construction of roads from blast-furnace slag stone. p. 314.
- Reis, L. Some problems of designing roads for industrial plants. p. 317.
- Vastagh, G. Lessons and guiding principles of the construction of earth dams on the basis of American experiences. Pt. 2. p. 319.

## LATVIA

### 12. GEOGRAPHY & GEOLOGY

#### PERIODICALS

Latvijas PSR Zinatnu akadēmija. Geoloģijas un derīgu izrakteņu institūts. TRUDY. Riga. [Papers issued by the Institute of Geology and Minerals, Latvian Academy of Sciences. In Russian]

No. 4, 1959.

- Danilans, I. Terminology and classification of post-glacial fresh-water time containing deposits and layers. p. 5.
- Hailik, O. Fresh-water lime containing deposits in southern Estonia and their agricultural evaluation. p. 25.
- Savickas, I. Some results of the research on fresh-water limestone in Lithuania with the purpose of utilizing it as a lime fertilizer. p. 35.
- Danilans, I. Conditions for Holocene fresh-water carbonate formations in Latvian territory. p. 41.
- Bartosh, T. About the stratigraphic adaptability and paleogeographical conditions for the accumulation of Holocene lime containing deposits. p. 57.
- Abolkašs, J. Conditions and course of Holocene carbonate formations in the largest Latvian deposits. p. 79.

## POLAND

### 12. GEOGRAPHY & GEOLOGY

#### PERIODICALS

**CZASOPISMO GEOGRAFICZNE.** (Polskie Towarzystwo Geograficzne) Wrocław. [Issued by the Polish

Geographical Society; with French summaries. Quarterly]

Recurrent features: Book reviews; Activities of the Society.

Vol. 31, no. 2, 1960.

- Birkenmajer, K. Significance of the Haligovce Klippe for the geology of the Pieniny Klippen Belt. p. 73.
- Narebski, W. The origin and postsedimentary changes of the gypsum-anhydrite deposit of Nowy Lad. p. 89.
- Prochazka, K., Wala, A. The dolomitic salt in the Wieliczka deposit. p. 105.
- Lozinski, J. Heavy minerals of sandstones of the Lower and Middle Cretaceous in the Pieniny Klippen Belt. p. 119.

**PRZEGLAD GEOGRAFICZNY. POLISH GEOGRAPHICAL REVIEW.** (Polska Akademia Nauk. Instytut Geografii) Warszawa. [Issued by the Institute of Geography, Polish Academy of Sciences; with English, French, and Russian summaries. Quarterly]

Recurrent features: Book reviews; Brief notes.

Suppl. to v. 30, 1958.

Index to v. 31, 1959.

Vol. 32, no. 1/2, 1960.

- Kondracki, J. Types of natural landscapes (geographical environment) in Poland. p. 23.
- Wieckowska, H. Geographical zones of the upper layer of underground waters. p. 35.
- Maruszczak, H., Trembaczowski, J. A tentative comparison of the Vidin region continental dunes in Bulgaria to the dunes on the Lublin Plateau in Poland. p. 163.
- Miszczak, A. Consolidation of land holdings as an agent of increased soil erosion. p. 179.
- Rotnicki, K. A review of problems concerning eskers. p. 191.

**Polskie Towarzystwo Geologiczne. ROCZNIK.** Krakow. [Annals of the Polish Geologic Society; with English and Russian summaries]

Vol. 29, no. 1, 1959.

- Kleczkowski, A. The Muschelkalk on the northern border of the Gory Swietokrzyskie west of Skarżysko-Kamienna. p. 3.
- Gerlach, T. The origin of mounds in Hale Długa in the Gorce Range. p. 85.
- Gilewska, S. Contribution to the knowledge of the karst development in the Middle Triassic metalliferous dolomites in Upper Silesia. p. 97.
- Siuta, J. On glei soil processes and ferruginous precipitates in the Kazimierz Dolny loess. p. 113.

### 16. TECHNOLOGY

**KOLTONSKI, WACLAW.** Propagacja fal ultradźwiękowych w skałach i jej praktyczne zastosowanie. [Wyd. 1.] Warszawa, Państwowe Wydawn. Naukowe, 1960. 59 p. [Propagation of ultrasonic waves in rocks and its application in practice. 1st ed. illus., bibl., diagrs., graphs, tables]

#### PERIODICALS

**ARCHIWUM GORNICTWA.** (Polska Akademia Nauk. Komitet Gornictwa) Warszawa. [Journal on mining and mineral resources issued by the Committee on Mining, Polish Academy of Sciences; with German and Russian summaries. Superseded in part Archiwum Gornictwa i Hutnictwa, 1956. See also Archiwum Hutnictwa. Quarterly]

Vol. 4, no. 4, 1959.

- Hiramatsu, Y.; Kokado, J. The coefficient of influences in calculating the sinking of horizontal deposits. In German. p. 285.
- Piatkowski, J. Variance of the ash content in samples of coal from the Silesian coal mines calculated on the basis of laboratory researches. p. 345.

Vol. 5, no. 1, 1960.

- Cybulski, W. Research on stone-dust side barriers. p. 3.
- Krupinski, B. The optimal size of a mine. p. 85.

## REFERENCE SECTION

- Salustowicz, A. The influence of the rate of excavation on the extent of deformation and value of stresses in a coal seam. In English. p. 91.
- Było, Z. The problem of pyrite and sulfonic groups in the process of spontaneous combustion of coal. p. 99.
- Piatkowski, J. A scheme of statistical control of ash content in Polish coal determined on a theoretical basis and laboratory practice. p. 177.
- Vol. 5, no. 2, 1960.
- Maczynski, J. A method of computing the pressure distribution in a slow flow of homogenous gas in ducts. In English. p. 147.
- Szpunar, K. The influence of time on the bending of ceiling deposits. In French. p. 157.
- Szklarski, L.; Gorecki, H. The planning of automatic-control systems in mining on the basis of typical logarithmic characteristic of amplitudes. p. 165.
- Korta, A. Investigations of the influence of the size of coal grain on the process of adsorption of p-cresol from aqueous solution. p. 193.
- Czerski, L.; Korta, A.; Lason, M. The capillary process of bituminous coal in the light of investigations on the adsorption of p-cresol from aqueous solution. p. 207.
- CEMENT, WAPNO, GIPS.** (Wydawnictwo "Budownictwo i Architektura") Krakow. [Publication on adhesives in the building industry issued by Building and Architectural Publications. Includes a supplement: Przegląd Bibliograficzny Materiałów Wiazacych, bibliography on adhesives. Monthly]
- Vol. 15 [i. e. 16] no. 7/8, July/Aug. 1960.
- Dlugosz, W.; Peszat, C. Influence of petrographic properties in the grindability of limestones of Leszna Gorna near Golezow. p. 212.
- Danzig. Instytut Morski. PRACE. SERIA I: HYDRO-TECHNIKA. Gdansk. [Papers on hydraulic engineering issued by the Marine Institute; with English summaries]
- No. 3, 1959.
- Slomianko, P. Fundamental problems of the protection of the Polish seacoast. p. 3.
- GORNICTWO.** (Akademia Gorniczo-Hutnicza w Krakowie) Krakow. [Papers on mining issued by the Academy of Mining and Metallurgy in Krakow; with English and Russian summaries]
- No. 6, 1959.
- Krajewski, R. The estimation of resources and the determination of the size of sampled deposits by using statistical methods. p. 27.
- Znanski, J. The mining of protective pillars in unfavorable conditions and configuration in relation to the elements of deposits. p. 49.
- Lisowski, A. The displacement of rock masses in the mining of slanting deposits. p. 55.
- Bednarski, M. An effective method of mining anticlinal seams in the case of simultaneous work on several levels. p. 71.
- GOSPODARKA WODNA.** (Naczelna Organizacja Techniczna) Warszawa. [Publication on water-power resources and hydraulic engineering issued by the Central Technical Organization. Monthly]
- Recurrent features: Bibliography; Book reviews.
- Vol. 20, no. 6, June 1960.
- Kollis, W. The time needed for the subsidence of a depression and its reach during the draining of foundations by lowering the ground waters. p. 250.
- Molisz, R.; Domanski, J.; Zwolinski, K. The identification of clay minerals by the diffraction of electrons. p. 281.
- Orkuszko, H.; Churski, T.; Karpinska, J. Peat bogs in the region of the karst lakes of the Usciwerze group in the Leczno-Wlodawa lake country. p. 285.
- NAFTA.** (Instytut Naftowy) Krakow. [Journal on petroleum engineering, processing, and management issued by the Petroleum Institute. Includes supplements: Przegląd Dokumentacyjny Nafty, documentation; Wiadomosci Naftowe, information bulletin; and Biuletyn Instytutu Naftowego, bulletin of the Institute. Monthly]
- Recurrent feature: Information from the Institute.
- Vol. 16, no. 6, June 1960.
- Wojnar, J. Wladyslaw Gomulka on the task of Polish science and petroleum problems. p. 149.
- Bozek, H.; Dzwinel, J. The purpose of using the method of telluric currents in the foremost part of the Sudetic monocline. p. 150.
- Michejda, J. Use of atomic energy for the exploitation of crude oil deposits. p. 161.
- Vol. 16, no. 7, July 1960.
- Kozlikowski, H. Problems of deep structures in the eastern Carpathian Flysch. p. 180.
- PRZEGLAD GEOLOGICZNY.** (Wydawnictwa Geologiczne) Warszawa. [Publication on economic geology issued by Geologic Publications. Monthly]
- Recurrent features: Organizational and legal problems; Brief notes; New publications: reviews and foreign periodicals; Standards and instructions.
- Vol. 8, no. 6, June 1960.
- Kveton, P. Organization of the geological survey in Czechoslovakia. p. 298.
- Knotek, Z.; Sirucek, V. Research on geologic raw materials in Czechoslovakia. p. 301.
- Skacel, J. Metalogeny of the eastern and Middle Sudeten. p. 306.
- Zezulka, J. Development of the raw-material basis of ore deposits in capitalist countries. p. 313.
- Masin, J. Aerial geophysical surveys in Czechoslovakia. p. 317.
- Foldyna, J. The aerial photography in the service of geology. p. 323.
- Stepanek, M. Television in geologic prospecting. p. 326.
- Pexa, L. The occurrence and possibilities of utilizing iodine and bromine waters of the Ostrava-Karvina region. p. 329.
- Pexa, L. The sand-and-gravel well filters. p. 331.
- Zdychynec, O. Socialist competition in the field of geologic prospecting. p. 333.
- Vol. 8, no. 7, July 1960.
- Mrozowski, M. July 22, 1960, in the State geologic service. p. 353.
- Olendski, W. The cause of the mineralization of artesian waters in the Masovian Basin. p. 355.
- Malinowski, J. Remarks on loess in the southern Lublin region as the local basis of ceramic raw material. p. 360.
- Ruskiewicz, M. Geologic structure and estimates of deposits of refractory quartzite sandstone of the western part of the Bieliny range. p. 366.
- Chmura, K. Characteristic properties of the Grochow serpentinites. p. 371.
- Kubicz, A. Vermiculite, its properties, occurrence, and use. p. 376.
- Przewlocki, K. New method of logging in the U. S. A. p. 380.
- Szwermer, R.; Borowy, R. The iodometric determination of sulfur in coal. p. 382.
- Jonca, E. The occurrence of granulite in the vicinity of Walbrzych. p. 384.
- Skompski, S. The most recent geologic formations in the vicinity of Gabin. p. 385.
- Gadomska, S. Quaternary bituminous shells. p. 387.
- Hudyma, P. For a proper organization of the repair of drilling machinery and installations. p. 388.
- Kowalski, W. Geologic engineering at the University of Moscow. p. 390.
- PRZEGLAD GORNICZY.** (Stowarzyszenie Naukowo-Techniczne Inzynierow i Technikow Gornictwa) Katowice. [Issued by the Scientific-Technical Association of Mining Engineers and Technicians. Includes supplements: Biuletyn Głownego Instytutu Gornictwa, bulletin of the Central Institute of Mining; Biuletyn Instytutu Mechanizacji Gornictwa, bulletin of the Institute of Mechanization in Mining; and Przegląd Dokumentacyjny Gornictwa, documentation. Monthly]
- Recurrent features: Current news; Foreign review; Polish standards.
- Vol. 15, no. 12, Dec. 1959.
- Salustowicz, A. The roof and floor pressure in brown-coal mines. p. 569.
- Lisowski, A. Developmental trends in methods and systems of mining thick seams in Upper Silesian coal mines. p. 572.
- Galanka, J. The use of abutment supports. p. 585.
- Izdebski, K.; Matuszewski, J.; Neyman, B. Heavy rock bursts in seams of the group 600 in Pstrowski and Sosnica collieries. p. 590.



## 16. TECHNOLOGY

- VODOPRIVREDA JUGOSLAVIJE. (Savezna komisija za vodoprivredu) Beograd. [Papers issued by the Federal Commission on Water Resources; with English, French, and Russian summaries]
- Vol. 2, no. 4/5, 1959.
- Blagojevic, B. Water-power bases; economic planning of the use of water power. p. 10.
- Davorin, B. Water-power bases. p. 14.
- Marjanov, M. Water-power bases. p. 17.
- Praprotnik, V. Power, energy, and economic problems in the use of complex water streams. p. 21.
- Bidovec, F. How to arrive at better hydrologic bases. p. 26.
- Bidovec, F. Characteristics of water; their outline in hydrologic reviews and publications. p. 31.
- Gorjackovski, V. Dimensioning the irrigation reservoirs. p. 39.
- Pavlovic, M. Contribution to the determination of the volume of water flowing in the Neretva River basin. p. 45.
- Grujic, N. Dynamic investigations of the constants of elasticity of the rocks where the future underground sections of the Dubrovnik Hydroelectric Plant will be built. p. 56.
- Guzina, B.; Popovic, V. Hydrologic analysis and investigations of stream sources in the vicinity of Niksic. p. 63.
- Igrutinovic, D. Hydrologic characteristics of the Jasenica River basin. p. 70.
- Jevremovic, M. Hydrologic connections between the Fatnik and Dabar plains and their effect on the Mirusa basin of the Trebisnica River. p. 77.
- Milovanovic, B. Geoelectric investigations of the alluvium of the Morava River. p. 86.
- Sarnavka, R. Methods of water research work in the Karst. p. 89.
- Torbarov, K. Some constant relations in the Karst; meaning of the results of water investigations in relation to the designing of hydrotechnic constructions. p. 95.
- Application of geophysical methods to the solution of some hydrotechnic problems in our country. p. 100.
- Praprotnik, V. Economical factor in water-power designs. p. 112.
- Domacinovic, Z. Investigations in the Sarajevo plain related to the water supply of Sarajevo. p. 116.
- Jankovic, C. Erosion from a geodynamic point of view and the importance of antierosion measures. p. 127.
- Blagojevic, B. Agriculture and irrigation farming. p. 132.
- Josimovic, D. Inland water and harbor transportation technique. p. 136.
- Petrovic, S. Waterways as a factor in the development of inland-water transportation. p. 138.
- Kujundzic, B., L. Jovanovic. Investigations on the permeability of water tunnels under pressure, using the diaphragm method. p. 144.
- Miljkovic, E. Joining the supply tunnel of the Jajce Hydroelectric Plant I with a natural lake under constant level. p. 153.
- Mikulec, S. Connecting joints of reinforced-concrete mains of large size. p. 159.
- Vol. 2, no. 6, 1959.
- Gavrilovic, S. Method of classifying stream flows and the new formulas for estimating torrential waters and their deposits. p. 3.
- Srebrenovic, D. Rainfall intensities and their application in the determination of the maximum water quantities. p. 15.
- Vukcevic, M. Movement of flood waves in the Morava River. p. 43.
- Milosavljevic, K. Intensity of showers on the profile Zemun Polje-Noví Belgrade - Belgrade. p. 59.
- B. B. 3d Congress of Hydraulic Engineers of Yugoslavia. p. 80.
- B. B. 2d Meeting of Experts for Irrigation and Drainage of Yugoslavia. p. 82.
- Milojevic, N. Hydrogeological terminology with corresponding English and Russian terms. [Supplement] p. [i-ii], 1.

- Vol. 16, no. 5, May 1960.
- Dziunikowski, K. The industrial exploitation of coal seams by underground gasification. p. 269.
- Bajer, M. The problem of natural fuel in countries belonging to the Organization for European Economic Cooperation and in the United States. p. 287.
- RUDY I METALE NIEZELAZNE. (Wydawnictwo Gorniczo-Hutnicze) Katowice. [Journal on the mining and processing of ores and the metallurgy of non-ferrous metals issued by Mining-Metallurgical Publications; with English, German, and Russian summaries. Monthly]
- Vol. 5, no. 6, June 1960.
- Gutowski, W. Possibilities of applying the sedimentation analysis for defining the grain structure of foundry dusts. p. 223.
- Konstantynowicz, E. Tectonic structure of the Goldberg basin. p. 232.
- Korszynski, R. Roof bolting in mining bolts. p. 237.
- Vol. 5, no. 7, July 1960.
- Gogolinski, H. Determination of dust grain compounds by microscopic analysis. p. 281.
- Galkiewicz, T. The origin of the Silesia-Krakow zinc and lead deposits according to F. Ekiert's concepts. p. 299.
- WIADOMOSCI NAFTOWE. (Stowarzyszenie Naukowo-Techniczne Inzynierow i Technikow Przemyslu Naftowego i Związku Zawodowego Gornikow Naftowcow) Krosno. [Publication on petroleum engineering and the petroleum industry for technical personnel issued by the Scientific-Technical Association of Engineers and Technicians of the Petroleum Industry and the Union of Petroleum Engineers. Monthly]
- Vol. 6, no. 5, May 1960.
- Kwolek, S. The exploitation of petroleum and gas in Poland. p. 98.
- Vol. 6, no. 6, June 1960.
- Karnkowski, P. The origin of crude oil and the formation of deposits. p. 121.

## YUGOSLAVIA

12. GEOGRAPHY & GEOLOGY  
PERIODICALS

- GEOGRAFSKI OBZORNİK. (Geografsko društvo Slovenije in Zemljepisni muzej Slovenije) Ljubljana. [Popular magazine issued by the Geographical Society of Slovenia and the Geographical Museum of Slovenia. Quarterly]
- Recurrent features: Geographical terminology; Organizational news.
- Vol. 7, no. 1/2, 1960.
- Moretti, F. Deposits and utilization of flint sand in Dolenjsko. p. 32.
- Srpska akademija nauka. Geografski institut. ZBORNIK RADOVA. Beograd. [Papers issued by the Geographic Institute, Serbian Academy of Sciences; with French summaries]
- No. 67, 1959.
- Farde, M. Relative power of the exceptional floods of rivers in the European Mediterranean regions. p. 1.
- Gerasimov, I. Problems of the Diluvial (Quaternary) period in the USSR. p. 19.
- Jovanovic, B. Oval cavities. p. 29.
- Milic, C. Contribution to the origin of red soils in the Suva Mountains. p. 89.
- Veljkovic, A. Relations between the heights and surfaces of longitudinal river profiles. p. 105.
- Atanackovic, B. Phytogeographic survey of the Ozren Mountains region and its vicinity. p. 121.

## RECENT TRANSLATIONS IN GEOLOGY

### A review of the Translation Services

The editors of International Geology Review begin, with this issue, a new service in the field of geology translations. There will be published each month a list of the new translations of geologic significance which have become available from sources other than IGR and the established cover-to-cover translation journals in geology. In doing this we expect to accomplish several purposes: 1) Inform geologists of the foreign literature in their field available in translation; 2) provide information necessary to avoid duplication of translation effort, and 3) advise geologists of the activities of the various organizations providing translations, or related services, in their field. Suggestions for improving this service will be welcomed.

Researchers interested in seeking out additional geologic literature from foreign languages should be aware of other potential sources. The following list may be of help. The AGI Translations Office will provide information on the availability of translations to the extent our facilities permit.

The following publications contain information on translations in geology or relate to the problem of acquiring or handling them:

Technical Translations, published twice a month by the -

Office of Technical Services,  
U. S. Department of Commerce,  
Washington 25, D. C.

LLU Translation Bulletin, published monthly by the -

Lending Library Unit,  
Department of Scientific and Industrial  
Research,  
20 Chester Terrace,  
London, N. W. 1, England.

Providing U. S. Scientists with Soviet Scientific Information, revised edition, May 1959, by the -

Office of Science Information Service,  
National Science Foundation,  
Washington 25, D. C.

List of Technical Translations, published at irregular intervals by -

The Library,  
National Research Council of Canada,  
Ottawa 2, Ontario, Canada

Bulletin d' Information Scientifiques et Techniques, published by the -

Commissariat a l'Energie atomique,  
S. A. R. L. DUNOD,  
92, rue Bonaparte,  
Paris (6<sup>e</sup>), France.

The sources for this first list were as follows:

Technical Translations; v. 4, nos. 9 and 10

LLU Translations Bulletin; v. 2, nos. 10 and 11.

List of Technical Translations; (National Research Council of Canada); Supp. 6, September 1960.

listings by -

Associated Technical Services, Inc.;  
List no. 80,  
Consultants Bureau Enterprises, Inc.  
no date.

The sources of these translations are identified by full name and address at the end of the list. Hereafter, readers may refer to current copies of Technical Translations, published by the Office of Technical Services, for addresses and prices.

Not included in the listings below are translations in the following six Soviet journals, which are published cover-to-cover beginning with the dates notes:

Doklady, Akademii Nauk, SSSR, ser. Geokhimiya, from 1956, CB;

Doklady, AN SSSR, ser. Geologiya, 1957, CB; from 1959, AGI;

Geokhimiya, from 1956, Geochemical Society;

Geologiya Neft (i Gaz), from 1958, Russian Review of Geology,  
212 S. Pitt St., Alexandria, Va.;

Izvestiya AN SSSR, ser. Geofizicheskaya, from 1957, American Geophysical Union;

Izvestiya AN SSSR, ser. Geologicheskaya, from 1958, AGI

LIST OF RECENT TRANSLATIONS  
IN GEOLOGY

- Ackermann, E., 1948: Quick soils and flow movement in landslides. *Zeitschrift der deutschen geologischen gesellschaft*, 100, pp. 427-466. NRC.
- Akopyan, Ts. G., 1955: Magnetic properties of rocks of Armenia. *AN Gruzinskoy SSR, Tiflis, Inst. Geofiziki Tr.*, v. 14, pp. 61-75. LC 60-23735.
- Alekshova, T. N., 1957: On the question of the division of the Ordovician system. *Sovetskaya Geologiya, USSR*, no. 55, pp. 93-113. LC 60-19872.
- Alekseyev, A. M., 1958: The PPMz-z accessory for intermediate magnetic recording in seismic prospecting. *Razvedochnaya i promyslovaya geofizika, USSR*, v. 22, p. 3-76. LC 60-23615.
- Amenitsky, N. A., Noskova, R. I., and Salomonovich, A. Ye., 1960: Radio image of the moon in the 8 mm range. *JPRS 5094*.
- Anonymous, 1960: Information of Soviet bloc International Geophysical Cooperations, 5 nos., Sept. 2-30, OTS, \$12 for series.
- \_\_\_\_\_, 1960. Rumanian nonferrous ore deposits. *Principali Data Monografica*, pp. V-42-V-47. *JPRS 5578*.
- \_\_\_\_\_, 1959: Iron deposits. *Information Africaine* no. 387, Aug. 6, p. 12. AMS, call no. Hc501.143, ord. OTS.
- \_\_\_\_\_, 1958: Problems of the North, compl. tr., 29 papers, AN SSSR, 400 pp. NRC.
- \_\_\_\_\_, 1958: Problems of the theory of destruction of rocks by explosives. *AN SSSR mining inst.* DI, TN7, E57, no. 311.
- \_\_\_\_\_, 1956: The geology of Uranium, suppl. 6, *Sov. Journ. of Atomic Energy*, 124 pp. CB.
- \_\_\_\_\_, 1927: The Svaran magnetic anomaly. *Geodezist.*, no. 8, pp. 47-49. *JPRS, R-105-N/23*.
- \_\_\_\_\_, (no date): Soviet research in crystallography, 1112 pp. from Soviet chemical journals, avail. complete or as separate papers. CB.
- Appolov, B. A., 1956: Caspian sea and its basin, Moscow, p. 1-121. LC 60-23763.
- Apresov, S. M., 1959: Certain theoretical aspects of the origin of petroleum in the formation of oil deposits. *Izv. Vysshikh. Ucheb. Zaved.*, *Neft i gaz* v. 2, no. 3, pp. 3-4. *ATS.*, FJ-2341.
- Arkharov, L. V., and Agamaliev, G. M., 1959: Relationship between porosity and oil saturation of a horizon and its electrical resistivity. *Izv. Vysshikh Ucheb. Zaved.*, *Neft i gaz*, v. 2, no. 4, pp. 7-9. *ATS, RJ2335*.
- Bekman, M. Yu. 1952: Materials for the quantitative characterization of the Black Sea bottom fauna at Karadag. *Karadag. biolog. stants.*, *Tr.* 1952, v. 2, pp. 50-67. LC 60-23773.
- Berg, L. S., 1947: Climate and life, Moscow, 2nd. edit., ch. 8. DI, QE 3, E57, no. 1.
- Bertaut, Felix, and Forrat, Francis, 1960: Structure of ferrimagnetic ferrite of rare earths. *Glastechnische berichte*, v. 33, no. 2, pp. 52-55. Ord. SLA, 60-18163.
- Borisov, A. A., 1959: On the paleoclimatic conditions of formations of the main pressure centres of the present climate of the earth. *Izv. Vses. Geograf. Obshch.* v. 91, pp. 255-265. *DSIR LLU, M.* 1789.
- Borisov, Yu. P., and Mukharsky, E. D., 1960: Determination of some characteristics of petroleum reservoirs by means of a formation tester. *Neftyanoye Khoz.* v. 38, no. 1, pp. 56-59. *ATS, RJ-2337*.
- Bulvanker, E. Z., 1952: Description of general excerpts from rugose corals from the Silurian of Podolia. *Tr. Vses. Nauch.-Issled. Geol. Inst. (VSEGEI), Ministerstvo geol.*, Moscow. DI, QE3, E57, no. 2.
- Chekalyuk, E. B., 1959: The selection of formulas for calculating the physical parameters of a gas reservoir from the pressure buildup in a shut-in well. *Gazovodya prom.*, v. 4, no. 11. *ATS, RJ-2338*.
- Chen, Chzhun-Syan, 1959: Calculation of the rate of infiltration of water in soil previously containing air. *Izv. Vysshikh Ucheb. Zaved.*, *Neft i gaz*, v. 2, no. 7, pp. 3-40. *ATS, RJ-2328*.
- Chukhrov, F. V., and Smolyaninova, N. N., 1956: Bertrandite from Kourad granite massif in Central Kazakhstan. *AN SSSR, Doklady*, v. 107, no. 7, pp. 579-580. LC 60-23740.
- Degtyarev, D. D., 1957: Guiding sign of certain Devonian corals from the mid-course of the River Aiy in Southern Urals. *Tr. Gorno-geolog. AN SSSR, Urals. filial*, no. 28. DI, QE3, E57, no. 18.
- Dobrolyuvova, T., 1958: Excerpts from the Lower Carboniferous colonial tetracorals from the Russian platform. *Tr. Paleontol. AN SSSR*, v. 52. DI, QE3, E57, no. 3.
- Dobryansky, A. F., 1949: Combustible shales of the U.S.S.R. Intra-bureau report, Bureau of Mines, July. DI, TN7, E57, no. 316.
- Dostálek, M., 1958: Action of bacteria on the release of oil from reservoirs. *Práce ústavu pro naftový* v. 9, pp. 29-44. *ATS, CJ-2354*.
- Dudykina, A. S., and Semenova, G. I., 1957: Lovozero and Khibina massifs--a rare-metal biogeochemical province. *Voprosy mineralogii geokhim. i genezisa mestorozhdenii redkikh elementov.*, no. 1, pp. 35-37. *AEC, 4185*.
- Ekstertsev, U. A., 1958: A study of the process of oil decomposition in microorganisms under anaerobic conditions. *Mikrobiologiya* v. 7, no. 5, pp. 626-633. *ATS, RJ-2356*.



## REFERENCE SECTION

- Fomichev, V. D., 1953: Excerpts from Rugosa corals and stratigraphy of Middle and Upper Carboniferous and Permian deposits of the Donets Basin. Tr. Vses. Nauch. -Issled. Geol. Inst., Ministerstva geol., Moscow. DI, QE3, E57, no. 4.
- Fomina, E. V., 1958: The problem of the structure of the test wall of some Visean foraminifera of the Moscow basin. Voprosy mikropaleontol. no. 2, pp. 121-123. ATS, RJ-2364.
- Feodosyenko, N. Y., and Groshevoy, G. V., 1953: A method of controlling the sensitivity and determination of frequency and amplitude responses of seismic receiving channels with the aid of magneto-electric generator. Izv. AN SSSR, ser. geofiz., no. 5, pp. 424-428. LC 60-23741.
- Finkelshtein, P. K., and Prudenko, V. A., 1958: A new method of determining indices of coking and rank of coals. Koks i khim, no. 3, pp. 6-12. DSIR LLU, M. 1755.
- Fourt, P. M., 1958: The operational value of iron ore. Annales des mines, Feb., pp. 93-111. IST.
- Galankina, E. A., and Bugrova, V. I., 1956: Assaying of ores and products of nonferrous metallurgy with the use of copper fusion. Sb. Nauk. Trudov, v. 12, pp. 45-51. NRC.
- Golovanov, I. M., 1959: A find of herntite in the Kurgashinkan deposit (Uzbek SSR), pp. 124-132, 398-401. ATS, RJ-2377.
- Gusein-Zade, M. A., 1956: Generalization of the problem of calculating the permeability of top and bottom layers of a formation during movement of a fluid through it. Tr. Moskv. neft. inst., no. 16, pp. 70-81. ATS, RJ-2333.
- Henriques, F. Goncalves: Solution of certain problems involving the hydroelectric installations on the Portuguese section of the Douro (Duero). Conference Mondiale de l'Energie, 17 pp. AMS; call no. EIF 356520, engl. tr.
- Iakubovich, A. L., 1958: Use of scintillation counters in radiometric equipment for prospecting for radioactive ore deposits. Bull. AN SSSR., ser. Fizich. v. 21, no. 4, 628 pp. CTT 1647.
- Ismaylov, K. A., 1957: Organic substance in the Cretaceous beds of North Kobystan, Southeastern Caucasus. Izv. AN Azerb. SSR, Baku, v. 14, no. 3, pp. 87-95. LC 60-23743.
- Ivaniya, V. A., 1958: On a new genus of coral from the lower Devonian of the Southwestern Kuzbass. Izv. Vysshikh Ucheb. Zaved., ser. Geol.-geograf., no. 2, pp. 121-124. DI, QE3, E57, no. 6.
- Janak, J., 1955: Prospecting for hydrocarbons based on chromatographic analysis of gases found in subsurface waters. Věstník ústředního ústavu geol. no. 30, 197-210. ATS, CJ-2359.
- Juránek, J., 1958: A contribution to the problem of the origin of  $C_1$ - $C_5$  hydrocarbons in samples of soil air in gas survey work. Prace ustava pro naftovy, v. 9, no. 37, pp. 57-79. ATS, CJ-2353.
- Kalashnikov, A. G., 1954: Determination of the magnetic susceptibility of rocks under field conditions. Izv. AN SSSR, ser. geofiz., no. 4, pp. 415-23. ATS, RJ-2351.
- Karchevskaya, Ye. P., Prospects of developing the Bazhenovo asbestos mines; Soviet non-ferrous metallurgy; selected translations, no. 13, JPRS 5438; OTS 60-41280.
- Kereyeva, G. D., 1958: Some ecologic morphae of Schwagerinas from the Bakmut trough of the Donets basin. Voprosy mikropaleontol., USSR, v. 2, no. 2, pp. 91-104. ATS 69-M42R.
- Khylstov, A. S., et al, 1959: The magnetic characteristics of NiCr ferrites. Tr. Izv. Vysshikh Ucheb. Zaved., fizika, no. 6, pp. 168-169. MDF, K-219.
- Klincharev, K. V., 1952: Materials for the quantitative characteristics of the Black Sea zoological plankton at Karadag. Karadagska biologichna stantsiya Tr. USSR, v. 12, pp. 78-95. LC 60-23766.
- Konoplina, O. R., 1956: The microfauna of the Upper Devonian deposits of the Olesko area (western Ukraine). AN USSR, Kiev, Dopovidi, no. 5, pp. 454-456. ATS-20M43U
- Kortsenshtein, V. N., 1954: Some new data on the tectonics of the central Cis-Caucasus in connection with hydrogeologic studies. Doklady, AN SSSR, v. 128, 162-180. ATS, RJ-2345.
- Kudryavtsev, N. A., 1959: Geologic proof of the deep origin of petroleum. Tr. Vessoyuz. Neftyan, Nauch. -issledovatel. Geologogaz-vedoch. Inst., no. 32, pp. 242-262.
- Lipina, O. A., 1959: Some data on the ontogeny of the Tournay order Ellidae (Foraminifera) Soc. geolog. of France Bull., ser. 7, v. 1, no. 7, pp. 649-650. ATS, 25M44F.
- Litvinenko, Ye. A., 1959: On the direction of degassing boreholes in steeply pitching beds. Izv. Vysshikh Ucheb. Zaved., Govnyy Zhur. no. 10, pp. 56-58. JPRS 5797.
- Malyuga, D. P., 1959. The application of the biogeochemical method in prospecting and exploration for copper and molybdenum ores. Razvedka i okhrana nedr., v. 25, no. 1, pp. 19-22. ATS, RJ-2360.
- Miloslavskaya, N. M., 1958: Temperature as a factor in the distribution of bivalve mollusks in Eastern Murman. no. 4, pp. 140-150. LLU, RTS 1637.
- Monténs, A., 1959: Application of radioisotopes in hydrology and hydraulics, pts. 1 and 2. Atompraxis, v. 5, pp. 91-93, 192-197. AEC NP, Tr. 469.

- Namiot, A. Yu., 1959: Changes in the gas composition of petroleum and gas deposits as a result of solution of gases in water. *Gasovaya prom.*, v. 4, no. 8, pp. 8-12. ATS, RJ-2344.
- Nedler, V. V., 1936: Quantitative determination of platinum and accompanying substances (satellites) in ores, ore slimes and tailings by a spectral method. *Zhur. Tekh. Fiz.*, v. 6, no. 3, pp. 553-560. NRC
- Nefedyev, A. A., 1957: New relief map of the moon. *Astronomichesky tsirkulyar*, Jan. 20, pp. 18-20. JPRS 3816.
- Ovchinnikov, N. V., 1960: Patterns in the alteration of the chemical composition of subsurface waters of the Azov-Kuban trough and the distribution of I and Br therein. *Izv. Vysshikh Ucheb. Zaved., Geol. i Razvedka*, v. 3, no. 1, pp. 134-138. ATS, 67M42R.
- Pătrut, I., 1959: Petrol si gaze, Bucharest, v. 10, no. 5, pp. 181-189. ATS, RU-2342.
- Pavlova, R. P., 1959: Establishment of boron content from the mineral composition of water. *Izv. Vysshikh Ucheb. Zaved. Neft i gaz*, v. 2, no. 8, p. 126. ATS, RJ2378.
- Pavlova, T. G., 1959: The Karsakpai massif of alkali and nepheline-syenites and its emplacement in the local tectonic structure, no. 10, pp. 78-91. LLU, RTS 152.
- Plakhotnik, A. F., 1959: Major scientific work on the Aral Sea; 50th anniversary of publication of L. S. Berg's monograph. *Sovet Kazakhstan*, no. 5, pp. 125-126. JPRS 4101.
- Reitlinger, E. A., 1950: Foraminifera of Middle Carboniferous deposits of the central part of the Russian platform (the family Fusulinidae excepted). *Tr. Inst. Geol., AN SSSR*, v. 126, Geol. ser. no. 47, pp. 1-12, 16, 18-19, 26-29, 87-89, 94-111. ATS, RJ-2365.
- Ryogo, Kubo, 1958: Report on some recent progress in the field of magnetic investigation in Tokyo. *Bull. AN SSSR*, v. 21, no. 8. CTT, 1186.
- Schiffers, Dr. Heinrich, 1960: Recent explorations in the Sahara. *Peterman's Mittheilungen*, v. 104, no. 1, pp. 1-19. AMS; call no. G1P47, Engl. tr., ord. OTS.
- Sharanov, I. V., 1952: Fauna of cliffs and stone pebbles in the Black Sea at Karadag. *Karadag. Biolog. Stants.*, Tr. v. 12, pp. 68-77. LC 60-23772.
- Sidorenko, A. K., 1957: Aspects of the development of drilling of deep boreholes in hard rocks. *Gornyy Zhurnal*, no. 14, pp. 10-14. LC 60-23811.
- Slepnev, Y. S., 1960: Relative age of rocks in the Khibina alkali massif, no. 4, pp. 89-95. LLU, RTS 1660.
- Slutskovsky, A. I., 1958: The dynamic range of vibrations recorded in seismic prospecting with reflected waves. *Vesesoyuz. Nauch. - Issledovatel. Inst. Geofiz. Metod., Obmen proizvodstvennym oryatom no. 22, Razvedochnaya i promyslovaya geofiz.*, pp. 76-94. ATS, RJ-2349.
- Smolkov, N. A., and Dai, Do-shen, 1959: Certain properties of yttrium and gadolinium garnet ferrites. *Izv. Vysshikh Ucheb. Zaved., fiziki*, v. 6, pp. 145-151. MDF, S-166.
- Su-Kuang, Li, 1959: Developments in geologic work in Communist China in the past decade. *K'o Hsueh T'ung Pao (Chinese People's Republic)* no. 18, pp. 586-93. JPRS-5090.
- Tokarev, A. N., and Shcherbakov, V., 1956: Radiohydrogeology. *Radiogidrogeologiya. AEC Tr-4100*, ord. OTS.
- Vallarino, E., and del Castillo, Canovas: Evaluation of the tidal energy resources along the coasts of Spain plus analyses. *Conference Mondiale de l'Energie. AMS; Call no. EIF 356523*, Engl. tr.
- Verbitskaya, Z. I., 1958: The spore-pollen complexes in Cretaceous depressions of the Suchan coal basin. *Tr. Lab. Geol. Uglya, AN SSSR*, no. 8, pp. 314-322. ATS, RJ-2369.
- Vorsin, A. N., and Doilnitsyn, Ye. F., 1959: A radio-frequency mass spectrometer (theory, calculation and design), edited by V. M. Klyarovskiy, *Geol. Inst. West. Siber. filial, AN SSSR, Moscow*, 76 pp. JPRS 5354, OTS 60-41217.
- Voskoboinikov, G. M., 1957: Intensity of  $\gamma$ -radiation in a homogeneous radiation medium. *Tr. Gorno-geol. Inst., AN SSSR*, v. 30, *Geofiz. sb. no. 2*, pp. 162-172. ATS, RJ-2352.

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USACRAPAC, PD	
ATS	Associated Technical Services, Inc. P. O. Box 271, East Orange, N. J.
CB	Consultants Bureau Enterprises, Inc. 227 West 17th Street, New York 11, N. Y.
CTT	Columbia Technical Translations 5 Vermont Avenue. White Plains, N. Y.

## REFERENCE SECTION

DI	Circulation Unit, Department of the Interior Central Library, Room 1149, Washington 25, D. C.
DSIR LLU	Lending Library Unit, Department of Scientific and Industrial Research, 20 Chester Terrace, London, N. W. 1, England.
IST	Iron and Steel Industries, 4 Grosvenor Gardens, London, S. W. 1, England
LC	Photoduplication Service, (microfilm and photo copies) Publication Board Project Library of Congress, Washington 25. D. C.
MDF	Morris D. Friedman, Inc. P. O. Box 35, New Newton 65, Mass.
NRC	The Library, National Research Council Ottawa 2, Ontario, Canada
SLA	Special Libraries Association, Translations Center The John Crerar Library, 86 East Randolph Street, Chicago 1, Illinois.

Deposit libraries for some of the documents listed may be found at the -

John Crerar Library (listed above),  
Carnegie Library, Pittsburgh, Pa.,  
Georgia Institute of Technology,  
Pennsylvania State University,  
University of California  
and the Library of Congress.

Prices of latest available translations are listed in *Technical Translations*, published twice monthly by the Office of Technical Services.

### GEOLOGIC TRANSLATION'S FROM THE PUBLIC LAW 480 PROGRAM OF THE NATIONAL SCIENCE FOUNDATION

Title I of the Agricultural Trade Development and Assistance Act of 1954 (Public Law 480), authorized the President to enter into agreements with friendly nations for the sale abroad of American surplus agricultural commodities for foreign currencies. As a result, there have accrued to the credit of the United States considerable sums in local currencies, usually referred to as "P. L. 480 funds."

An amendment enacted on June 30, 1958, made it possible for Government agencies to use P. L. 480 funds "to collect, collate, translate, abstract, and disseminate scientific and

technological information and to conduct and support scientific activities overseas."

In July 1958, the Bureau of the Budget requested the National Science Foundation to assume responsibility for testifying before the Senate Appropriations Committee on behalf of all interested Government agencies in order to secure an appropriation of P. L. 480 funds to be spent for translation overseas of foreign scientific literature. Following this testimony the Congress appropriated \$1,200,000 for the purchase of these currencies from the Treasury Department.

In January 1959, the Foundation was assigned the responsibility for coordinating the budgetary requests of Federal agencies interested in acquiring foreign translations, and conducting the acquisitions programs on their behalf. Initially these agencies included the Atomic Energy Commission, the Departments of Agriculture and Interior, and the National Library of Medicine. In cooperation with these agencies the Foundation arrived at a mutually satisfactory division of the available foreign currency, and an agreement on the languages to be covered. It was also mutually agreed that these translations would be made available to the scientific community through the Federal agencies participating in the program, and through the Office of Technical Services, U. S. Department of Commerce, which would also announce them in Technical Translations.

In addition to the four agencies listed above, the Department of Commerce and Smithsonian Institution are participating in the FY 1961 program, and the National Aeronautics and Space Administration will join in the program proposed for FY 1962.

The first three contracts to be signed were with Israel, Poland and Yugoslavia. Under the contract signed in April 1959 with Israel, approximately 27,500 pages of noncurrent scientific and technical journals, serials, books, monographs and selected articles from Russian and other Eastern European languages are being translated, edited and printed. From a later allocation for continuation of the Israel program, about 24,000 additional pages of material will be translated, edited and printed. Under contract signed in August 1959 with Poland, 19,000 pages of Polish scientific and technical literature will be translated, edited and printed. The Yugoslav contact, May 1960, calls for translation of 20,000 pages of Serbo-Croatian and other European scientific literature.

Concepts underlying the P. L. 480 translation program differ in several particulars from those on which the dollar-supported domestic translation program is founded:

1. Selections of publications for translation



are made by government research scientists.

2. The countries concerned have an interest in translating into English their own national scientific production, and their scientists furnish to American government scientists lists of materials which they consider of scientific importance.

In carrying out its functions under the program, the National Science Foundation assists participating Government agencies in the selection of material to be translated. Final selections is made by government scientists on the basis of the needs of their agencies and the requirements of the scientific community. Lists submitted by agencies are checked by the Foundation for duplicate requests and commercial publishers are consulted to determine their interest in the material recommended.

Geologists are urged to review the foreign literature in their field and recommend that which contributes new, significant information of the science, and forward such recommendations to the Translations Office of the American Geological Institute. That material which is deemed suitable for translation under this program will be funneled to the appropriate government agency for their action.

By early December 1960, three lists of translations completed or in process of translation had been issued by the National Science Foundation. Completed translations are obtainable from the Office of Technical Services, Department of Commerce, Washington 25, D. C., at a minimum cost of 50 cents for short articles or an approximate cost of 1-cent per page for articles and books of more than 50 pages. Translations should be ordered by OTS or AEC identification numbers. Future translations completed under the Public Law 480 program of interest to geologists will be reported in the regular listing of recently completed translations in this Reference Section of International Geology Review. To better illustrate the scope of translations in geology and related fields to have been included in the P. L. 480 program, pertinent items from the first three lists, dated August 27, October 10, and December 7, 1960, are as follows:

- Avsyuk, G. A., Markov, K. K., and Shumsky, P. A., 1956, Cold wasteland in the Antarctic Continent. *Izvestiya Akademii Nauk SSSR, Seriya geograficheskaya* (Moscow), no. 4, pp. 16-25. OTS 60-21094. \$0.50.
- Bagramyan, G. A., 1958, The Lining of irrigation canals. *Gidrotekhnika i melioratsiya* (Moscow), v. VIII, pp. 20-27. Russian. OTS 60-21108. \$0.50.
- Dadaev, G. T., 1958, Ramming roller for soil compaction. *Gidrotekhnika i melioratsiya* (Moscow), v. X, no. 3, pp. 18-25. OTS 60-21158. \$0.50.
- Denisov, N. Ya., 1957, Engineering geology and hydrogeology. Selected sections from

- State Publishing House for architecture and building literature, Moscow, pp. 137-143, 210-276, 287-301. 107 pp. OTS 60-21861. \$1.00.
- Glukhov, I. G., 1956, Seepage of water from canals in loess formations and subsidence phenomena in irrigated areas. *Gidrotekhnika i melioratsiya* (Moscow), v. VIII, no. 10, pp. 9-18. OTS 60-21152. \$0.50.
- Gorchakov, M. P., Puzrevskaya, T. N., 1956, Overflow rock-fill dams of the type suggested by Prof. N. P. Puzrevsky. *Gidrotekhnika i melioratsiya* (Moscow), v. VIII, no. 2, pp. 33-42. 15 pp. OTS 60-21824. \$0.50.
- Jarocki, W., 1958, Empirical method for the determination of the quantity of sediment transport. *Archiwum Hydrotechniki* (Archives of Hydrotechnics), v. 5, no. 2, pp. 251-266. From Polish. 11 pp. OTS 60-21521. \$0.50.
- Krakiwicz, Stanislaw, 1958, Protection against dangerous shocks in rural installations. *Mechanizacja Rolnictwa* (Journal of the Ministry of Agriculture, Dept. of Mechanization of Agriculture), v. 5, no. 7, pp. 14-16. 4 pp. From Polish. OTS 60-21238. \$0.50.
- Lisitsyn, A. P., and Zhivago, A. V., 1958, Bottom Relief and sediments of the southern part of the Indian Ocean. *Izvestiya Akademii Nauk SSSR, Seriya geograficheskaya* (Moscow), no. 2, pp. 9-21. OTS 60-21103. \$0.50.
- Ibid., no. 3, 1958, pp. 22-36. OTS 60-21104. \$0.50.
- Lisitsyn, A. P., and Zhivago, A. V., 1957, New data on the relief of the bottom and sediments of the seas of the eastern Antarctic. *Akademii nauk SSSR, Seriya geograficheskaya* (Moscow), no. 1: 19-35. OTS 60-21105. \$0.50.
- Ministry of Electric Power Stations of the USSR, 1952, Code of practice for the design of hydraulic structures. *Hydraulic computation of weirs*. Gosenergoizdat, Moscow. 76 pp. OTS 60-21864. \$0.75.
- Ministry of Electric Power Stations of the USSR, no date, Code of practice for the design of hydraulic structures. *Underground contour of Damson non-rocky foundations*. 91 pp. OTS 60-21157. \$1.00.
- Presnyakova, G. A., 1956, Classification of eroded soils. *Pochvovedenie*, Moscow, no. 10, pp. 69-90. Russian. OTS 60-21122. \$0.50.
- Prusinkiewicz, Zbigniew, 1954, A colorimetric field method for determining the moisture content of soils and ground. *Roczniki Nauk Rolniczych* (Polish Agricultural Annual), v. 70: Ser. a, no. 1. From Polish. 18 pp. OTS 60-21526. \$0.50.
- Romanov, V. V., 1956, Hydrophysical methods of calculating the water balance of bogs. *Pochvovedenie*, Moscow, no. 8, pp. 49-56. Russian. OTS 60-21121. \$0.50.
- Rubinshtein, A. L., 1958, Principles of engineering calculations for loess soils

## REFERENCE SECTION

- deformation under irrigation installations. *Gidrotekhnika i melioratsiya* (Moscow), no. 8, pp. 20-27. OTS 60-21159. \$0.50.
- Shnitnikov, D. V., 1951, Discussion of problems of soil consolidation and of shearing resistance of soils. *Gidrotechnicheskoye stroitelstvo* (Moscow), v. 9, pp. 38-43. 12pp. OTS 60-51077. \$0.50.
- Yushmanov, O. L., 1956, Sand traps on canals. *Gidrotekhnika i melioratsiya*, Moscow, no. 1, pp. 28-34. Russian. OTS 60-21107. \$0.50.
- Zamarin, E. A., 1959, Seepage through foundations of earth dams. *Gidrotekhnika i melioratsiya* (Moscow), v. 11, no. 4, pp. 22-25. 5 pp. OTS 60-21829. \$0.50.













